

PUBLIC HEALTH CHEMICAL ANALYSIS

BY

ROBERT C. FREDERICK

ANALYTICAL ASSISTANT TO THE PROFESSOR OF HYGIENE, ROYAL
NAVAL MEDICAL SCHOOL, ROYAL NAVAL COLLEGE, GREENWICH

AND

AQUILA FORSTER

Ph.D., M.Sc., A.I.C.

RESEARCH CHEMIST, RESEARCH DEPARTMENT, ROYAL ARSENAL
WOOLWICH, FORMERLY ASSISTANT LECTURER IN CHEMISTRY
ARMSTRONG COLLEGE, DURHAM UNIVERSITY

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INTRODUCTORY

GRAVIMETRIC ANALYSES

IN gravimetric analysis the amount of a substance in a weighed sample of the material under examination is completely separated and weighed in a pure form, either as such or as some derivative. Weighing, then, is the chief feature of gravimetric analysis, and requires the best balances and the greatest possible accuracy.

The Balance

For gravimetric analysis a balance should be sensitive to a tenth of a milligramme with a 200 gm. load. It should be protected from vibration, sunlight, heat, dust, and fumes. The level is adjusted by means of the screw legs, and the zero must be frequently checked and readjusted if necessary. Drying agents, such as calcium chloride, are often placed inside the balance, but the advantage of these is questionable; a stick of caustic soda in a jar protects the balance from the acid fumes common to a laboratory. All weighings are made at ordinary temperature; small variations in temperature between different weighings may introduce considerable error. If the object to be weighed has previously been heated, it must be placed in a desiccator to become cold before weighing; some chemists, in addition, allow it to stand in the balance case for a few minutes.

The weights are introduced on to the right-hand pan through a side door of the case with the front window closed; if no side door is provided, the front window is only partially opened. During the adjustment of the rider the case must be entirely closed to exclude air draughts. Too much attention cannot be given to the cleanliness of the balance; the pans and floor must be dusted frequently with a camel-hair brush. A highly

sensitive balance will require very gentle treatment if its accuracy is to be preserved.

The balance must be at rest during the moving of weights or objects on the pans. The arrestment of the balance is made gently as the pointer approaches the central position, and jerking is avoided. The same length of swing is used as nearly as possible during all weighings.

Filtration

Filtration, though a simple operation, necessitates careful attention to detail to ensure accuracy.

The filter funnels usually supplied are not all adapted for rapid efficient filtration. The cone of the funnel should be exactly 60° , so as to allow a folded filter to fit tightly against the sides of the funnel. Funnels are tested in this way, and those with air gaps between the paper and funnel are rejected. The paper is folded carefully so that no part overlaps.

Filtration and washing is more rapid with hot liquids than with cold. The liquid to be filtered is directed down a glass rod into the cone of the filter; if the liquid is being transferred from a beaker the rod is placed conveniently across the beaker and firmly clamped in that position by the thumb of the left hand, the fingers pressing on the base of the beaker. The beaker is rinsed with a wash bottle held in the right hand.

The filter must not be filled beyond a quarter of an inch of the top either during the filtration or washing of the residue. The washing is controlled by testing the filtrate to ensure complete removal of soluble matter. The filter is allowed to drain completely between each washing. Precipitate adhering to the beaker is removed by rubbing with a rod tipped with a piece of rubber tubing. Although previous drying of the filter paper and incineration after separation of the bulk of the precipitate is often recommended, it is really unnecessary except with fusible substances, and much time can be saved by transferring the wet filter paper to a weighed crucible and igniting directly over a Bunsen burner or in a muffle furnace. When dealing with fusible precipitates it is necessary to separate the precipitate from the paper before incineration, and to decarbonise in the crucible at a low temperature before adding the precipitate,

which, meanwhile, has been retained on a covered clock glass. Precipitates which may have suffered reduction by the ignited paper require to be further treated; dilute reagents are added to the cooled crucible in these cases, and the ignition is repeated after drying on a hot plate.

Filtration through Gooch crucibles (Fig. 1) is a convenient and accurate method of separation. Asbestos pulp is most commonly used, and is previously freed from soluble matter by boiling alternately with dilute alkali and acid, and washing. A small pad of the asbestos is prepared by pouring a little of the thin pulp into the crucible, and is then covered with a perforated disc; the crucible is ignited and weighed. The crucible is affixed on to a filter flask (Fig. 2) and reduced pressure is applied during the filtration. After washing, the crucible is dried at 100° C. and weighed; in some cases it is necessary to dry at a higher temperature or to ignite.

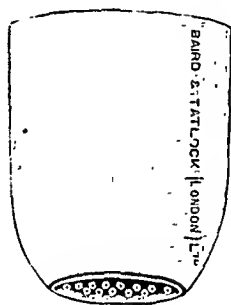


Fig. 1.

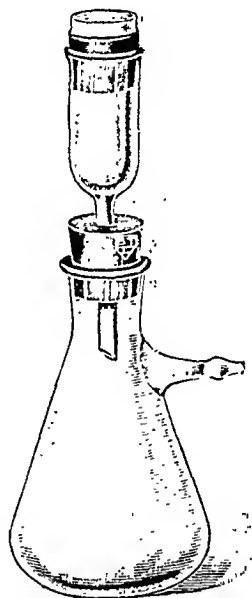


Fig. 2.

It is often better with small quantities of an infusible precipitate, such as barium sulphate, to weigh direct on the pan of the balance. In such a case the precipitate is gently brushed out of the crucible with a camel-hair brush on to the pan and weighed.

Platinum Vessels

Platinum dishes are particularly useful as evaporating basins and ignition crucibles. Platinum forms fusible alloys with the base metals, consequently it is never heated on gauze, but on pipe-clay or silica triangles or asbestos sheets, and tongs for their handling are tipped with platinum foil or wire. Silver, lead, tin, bismuth, arsenic, and antimony compounds, caustic

alkalies, baryta, alkaline nitrates, and substances evolving chlorine, iodine or sulphur, must not be heated on platinum.

Specific Gravity

The specific gravity of a substance is the relative weight of the substance compared with the weight of the same volume of distilled water at a standard temperature. For analytical purposes 15.5°C. is taken as the standard temperature.

The most accurate estimation of the specific gravity of a liquid is made by direct weighing in a specific gravity bottle or a pycnometer. A very convenient and an almost equally accurate determination can be effected with the Westphal balance; on account of its rapidity it is largely used in public health work. Hydrometers give rapid though not very accurate gravity determinations; most give direct readings, but some are graduated in Twaddle, Baumé, and other scales, which can be converted into specific gravity by means of tables or simple calculation. Lactometers and urinometers are provided with scales whereby the determination for which they are specially designed can be read directly. As the specific gravity of a liquid varies with temperature, the temperature is recorded with each determination, and a temperature correction made if a standard is to be referred to.

VOLUMETRIC ANALYSES

Although volumetric analyses are often contrasted with gravimetric analyses they are really a development of the latter, for they depend on the gravimetric estimations whereby the quantitative relationships in which the substances react with each other have been determined.

Volumetric analysis determines the concentration of a particular substance in a given solution, and from this, when the solution contains a known weight of a sample, the amount of the substance in the sample can be calculated. The measurements being made in volumes, these determinations are more rapid than those of gravimetric analysis.

In a reaction between two substances, the amounts of each by weight which take part can be calculated from the reaction

equation. When solutions of these substances are taken, the volumes of these which enter into complete chemical reaction with each other contain the reacting substances respectively in the proportion of these reacting weights. If the concentration of one of these be known, then from this proportion the weight of substance in the other, which reacts with a given volume of the solution of the first, can be calculated. This, then, is the amount of the second substance contained in that volume of its solution which actually does react with the given volume of the first; this is the concentration of the second solution. In all such calculations three determinants are necessary: first, the quantitative data of the reaction employed; second, the volumes of the reagent solutions which enter into complete chemical reaction; and the third, the concentration of one of the solutions.

The essentials of a volumetric process consist of the finding of these determinants, *e.g.* a solution, the strength of which requires to be estimated, is treated with a solution of known concentration of a substance with which it enters into a known reaction. The volumes which enter into complete reaction with each other are found by experiment. The concentration of the standard solution gives the weight of the substance in the volume employed. From this, by means of the reacting weights given in the equation of the reaction, the weight of the examined substance which reacts with this weight is obtained. This, then, is contained in the volume of the examined solution which has been found experimentally to react quantitatively with the given standard solution, and thus the concentration of the examined substance is determined. All calculations of volumetric analysis are on the same principle; they amount to a proportion in which the ratio is the weights provided in the reaction equation.

Standard and Normal Solutions

A standard solution is one the concentration of which is accurately known. This can be prepared by dissolving a known quantity of a substance in water and making the solution to a definite volume, or the concentration of a solution can be determined experimentally. For these purposes measuring

flasks are used, convenient capacities being 1000, 500, 250, and 100 cubic centimetres (cc.). An etched mark on the neck indicates the height to which the flask, at ordinary temperature (15.5°C. or 60°F.), must be filled to contain the stated volume of solution. The lower part of the meniscus is used in reading, the eye being brought to the same level to avoid parallax; the meniscus is more clearly defined by placing the finger behind the level. *Standard solutions are always made with distilled water* and thoroughly mixed by pouring from the flask into a dry vessel and back again several times with shaking. It is usual to prepare a stock of standard solution to serve a large number of similar analyses, in which case it is transferred to an appropriately labelled stock bottle.

Normal Solutions

If the concentration of solutions which react with each other are in the proportion of the reacting weights, it is clear that equal volumes of both solutions will enter into complete chemical reaction; therefore, if standard solutions are made relative to each other in concentration in these proportions, they will be equivalent to each other by volume. In all chemical reactions it is the equivalent weights of the reacting radicals which react quantitatively. The weight containing the equivalent of the reacting radicals in grammes, per litre of solution, has been taken as a suitable standard whereby concentrations of solutions can be made proportional to their reacting weights, and thus universally equivalent to each other.

A normal solution contains the equivalent of the reacting radical in grammes per litre, *e.g.* in the case of acids, 1.008 grammes of hydrogen per litre.

With normal solutions, reference to the reaction equation can be dispensed with as they embody the quantitative data on which the equations themselves are constructed. If a given volume of a normal solution has been found to react with a certain volume of an examined solution, it is sufficient to remember that this volume of normal solution would react with its own volume of examined solution if the latter were normal. Such a normal solution would contain the equivalent

of the reacting radical of the substance in grammes per litre, from which, and the volume indicated, the weight of the substance in the volume examined can be deduced.

Volume Determinations

To determine the volumes of the standard and examined solutions which react with each other, a given volume of one is introduced into a suitable vessel to which the second is gradually added until complete reaction is indicated, arrangements being provided whereby the exact volume added can be observed. For the first, pipettes are used which are made to deliver from an etched mark, definite volumes at 15.5° C., such as 100, 50, 25, and 10 cc. Before use they are rinsed out with the liquid with which they are to be filled. Heating of the bulb by holding in the hand is avoided. The liquid is allowed to run out from the pipette with the tip touching the receiving vessel; it is allowed to drain for fifteen seconds, and the vessel is then withdrawn. Contaminations from the mouth can be guarded against by inserting a plug of cotton wool in the mouthpiece or by aspirating through a side tube or a length of rubber tubing provided with a clip.

A given volume of one of the solutions having been pipetted into a vessel such as a beaker, basin, or flask, the other is run into it from a burette. The laboratory equipment will include a number of 50 cc. burettes, of which one at least should be a standard burette. Generally the blue-lined variety of burette is recommended for accurate reading. Burettes must be cleaned frequently with concentrated nitric acid, and the dry tap lubricated with a thin film of resin cerate. The burette is filled and rinsed with the solution before filling. The solution is now added from the burette to the pipetted solution in the reaction vessel until the reaction is complete. This is shown by means of indicators.

Indicators

Some chemical reactions can be followed by the colour changes effected in the reagents themselves; for instance, potassium permanganate serves as its own indicator. In other reactions in which no such colour change is manifest, the point

of complete reaction is seen by means of the colour changes of an indicator which has been added. An important class of indicators consists of organic substances which give characteristic colour contrasts with acids and alkalies. The following are those commonly used :—

LITMUS

Red with acids ; blue with alkalies. It cannot be used in the presence of carbon dioxide or sulphuretted hydrogen.

METHYL ORANGE

Red with acids ; orange-yellow with alkalies. It cannot be used with organic acids, but is extremely sensitive to mineral acids. It is not affected by carbon dioxide, hydrocyanic acid, and sulphuretted hydrogen.

PHENOLPHTHALEIN

Colourless with acids ; purple-red with alkalies. It cannot be used with ammonia, sulphuretted hydrogen, or carbon dioxide. It is commonly used in the titration of acids with baryta, or carbonate-free sodium hydroxide solutions, and is very suitable for organic acid titrations.

METHYL RED

Scarlet with acids ; lemon-yellow with alkalies. It can be used with ammonia, but not with carbon dioxide or sulphuretted hydrogen.

The most sensitive effects are obtained with the minimum amount of indicator which produces a perceptible colour change.

If the reaction vessel is of glass it is stood on a white plate to facilitate colour observations ; it is sometimes advantageous to gauge the end-point by comparison with approximately the same dilution of indicator in boiled distilled water.

Titration is continued with stirring or shaking until the indicator colour change occurs and remains permanent.

Standardisation of Solutions

Sodium carbonate, oxalic acid and succinic acid, crystallised potassium hydrogen tartarate, and Iceland spar are used

for standardising acid and alkali solutions. The strength of a solution may be stated in grammes per litre, or by a factor which gives the proportionate strength to the normal.

Sodium carbonate is the most satisfactory standard of reference for general use. Pure anhydrous sodium carbonate may be obtained, but it is better to prepare it fresh from the bicarbonate. It is washed with cold water to remove sulphates and chlorides, dried, and heated in a hot-air oven, in a platinum basin to 240°C . for $1\frac{3}{4}$ to 2 hours; the causticising which may take place is negligible. The sodium carbonate is cooled in a desiccator and transferred to a weighing bottle; the stopper should fit *over* the mouth.

25 cc. of a normal acid solution neutralises 1.325 gm. of sodium carbonate. Quantities approximating to this amount are introduced directly from the weighing bottle into three or four flasks and their weights are given by difference. These portions are dissolved in water, and titrated with the acid, using methyl orange indicator. The titrations should indicate the same strength for the acid.

EXAMPLE :

1.2000 gm. of sodium carbonate required 20.2 cc. of HCl solution,
and 53.00 " " " " = 1 litre of normal HCl.

$$\therefore 1.2000 \text{ " " " " } = \frac{1000 \times 1.2}{53} = 22.64 \text{ cc. N. HCl.}$$

$$\text{Strength of hydrochloric acid solution} = \frac{22.64}{20.2} \text{ N.} = 1.12 \text{ N.}$$

It is always necessary to compare the standardisation with an independent reagent. Oxalic acid has often been used, but there are difficulties associated with the drying and the water of crystallisation. Succinic acid or potassium hydrogen tartarate can be obtained in a pure anhydrous condition by means of crystallisation, and are very suitable for the purpose. The process is as described above; care must be taken to dry and powder the materials thoroughly previous to weighing. Another method is to convert sodium or potassium oxalate into carbonate by heating, and to standardise the acid by titration with the alkalinity produced. Potassium oxalate is obtained pure by crystallisation, is ground, and dried at 100°C .

Small portions (2 to 2.5 gm.) are accurately weighed into platinum dishes and gently incinerated. The ash is dissolved in hot water and titrated with the acid, using methyl orange as indicator. The formation of caustic potash during heating is immaterial, as long as the calculation is based on the potassium oxalate originally taken.

Preparation of Normal Solutions

Normal solutions are prepared where possible by direct weighing; in other cases, such as sulphuric and hydrochloric acids, and sodium hydroxide, slightly stronger solutions than normal are made, standardised by titration, and diluted to the required volume to give a normal solution. A confirmatory standardisation as described above is then carried out on the final solution.

Normal Sulphuric and Hydrochloric Acids

Pure sulphuric acid of commerce varies from 94 to 96 per cent. strength, and is of sp. gr. 1.84. As 49 gm. of sulphuric acid are contained in 1 litre of normal solution, 29 to 30 cc. are added gradually to about 500 cc. of water in a flask; the mixture is cooled and diluted to 1 litre with water. The mixed solution is titrated against a standard alkali or a weighed portion of sodium carbonate.

Pure fuming hydrochloric acid of commerce contains about 35 gm. of hydrochloric acid in 100 cc. 110 to 120 cc. are diluted to 1 litre and standardised.

These solutions will be found to be stronger than normal, and must be diluted accordingly; for instance, in the example quoted in the foregoing:

20.2 cc. of HCl solution = 22.6 cc. of normal acid.

∴ each 20.2 cc. of HCl solution requires to be made to 22.6 cc. to be normal.

The volume of the solution available is measured, and the increase in volume necessary to dilute it to the normal strength is calculated as shown below. The addition is made, and the diluted solution is then well mixed and standardised exactly with sodium carbonate or sodium oxalate as described.

EXAMPLE :

Volume of solution is 963 cc.

$$\therefore \text{Volume to which this must be diluted to be normal} = \frac{963 \times 22.6}{20.2} = 1084 \text{ cc.}$$

Distilled water to be added = $1084 - 963 = 121$ cc.

Normal Sodium Carbonate Solution

53.00 gm. of sodium carbonate is dissolved in a small quantity of distilled water, and diluted in a graduated flask to 1 litre.

Normal Sodium Hydroxide Solution

45 gm. of sodium hydroxide is dissolved in about a litre of water. The solution is standardised and diluted as requisite.

The following table gives the molecular and equivalent weights of substances most commonly employed in volumetric analysis :

Substance.	Formula.	Molecular Weight. (Oxygen=16.)	Equivalent Weight.
Sulphuric acid	H_2SO_4	98.08	49.04
Hydrochloric acid	HCl	36.47	36.47
Nitric acid	HNO_3	63.02	63.02
Oxalic acid	$\text{C}_2\text{H}_2\text{O}_4, 2\text{H}_2\text{O}$	126.06	63.03
Acetic acid	$\text{C}_2\text{H}_4\text{O}_2$	60.04	60.04
Lactic acid	$\text{C}_3\text{H}_6\text{O}_3$	90.07	90.07
Succinic acid	$\text{C}_4\text{H}_6\text{O}_4$	118.07	59.03
Boric acid	H_3BO_3	61.92	61.92
Sodium hydroxide	NaOH	40.01	40.01
Sodium carbonate	Na_2CO_3	106.01	53.00
Sodium bicarbonate	NaHCO_3	84.02	84.02
Potassium hydroxide	KOH	56.11	56.11
Potassium carbonate	K_2CO_3	138.21	69.10
Barium hydroxide	$\text{Ba}(\text{OH})_2, 8\text{H}_2\text{O}$	315.52	157.76
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	74.09	37.04
Calcium oxide	CaO	56.07	28.03
Calcium carbonate	CaCO_3	100.08	50.04
Silver nitrate	AgNO_3	169.89	169.89
Sodium chloride	NaCl	58.46	58.46
Potassium permanganate	$\text{K}_2\text{Mn}_2\text{O}_8$	316.06	31.61
Sodium thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3, 5\text{H}_2\text{O}$	248.20	248.20
Arsenious acid	As_2O_3	197.92	49.48
Iodine	I	(Atomic Weight) 126.92	126.92

General Notes on Acidimetry and Alkalimetry

There is no advantage, beyond ease of calculation, in making solutions exactly normal, but the analyst is advised to work with solutions as far as possible of about normal strength; tenth normal (N/10) solutions require very frequent restandardisation, as they are liable to change in concentration. Discretion requires to be exercised in the use of the indicators; methyl orange gives an exact end-point only when passing from acid to alkali, not from alkali to acid. Phenolphthalein gives a sensitive colour change, and if necessary it can be used with carbonates if the titration is carried out in boiling solution. When used in the cold for other estimations any water employed must be freed from carbon dioxide by previous boiling.

The methods of direct titration of acids and alkalies have been indicated in the foregoing pages. The following are general processes of analysis in special cases.

AMMONIA

Ammonia is separated by distillation and may be titrated in the distillate, using litmus as indicator. (For example see estimation of nitrogen, page 174.)

ALKALI CARBONATES

Alkali carbonates can be titrated against standard acids, using methyl orange, or may be acidified with a measured amount of standard acid, and the excess of acid estimated by standard sodium or barium hydroxide, after boiling the solution to remove carbon dioxide, using phenolphthalein as indicator.

ALKALINE EARTHS AND CARBONATES

These are dissolved in excess of standard acid, and after boiling to remove carbon dioxide, titrated with sodium hydroxide as above.

CAUSTIC SODA AND SODIUM CARBONATE IN MIXTURE

The total alkalinity is estimated by titration with standard acid, using methyl orange indicator. To a fresh volume an excess of barium chloride solution is added to precipitate the carbonate as barium carbonate; the solution is filtered with thorough washing and the filtrate is titrated with standard acid and the alkalinity is calculated as sodium hydroxide. The figure of this titration is deducted from that found in the first titration and the difference is calculated to sodium carbonate.

SODIUM CARBONATE AND BICARBONATE IN MIXTURE

The total alkalinity is estimated as before. A measured volume of standard sodium hydroxide solution is added to combine with the bicarbonate, and the excess is determined after removing the carbonate with barium chloride as described. The amount of sodium hydroxide neutralised gives the bicarbonate. The sodium carbonate is obtained by difference.

Example of Calculation:

(1) With Standard Solutions.

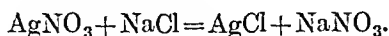
In a given solution of sodium chloride it is required to determine the weight of chlorine per cubic centimetre. The solution is titrated with a solution of silver nitrate containing 5 gm. per litre.

29.0 cc. of silver nitrate solution was found necessary to react with 25 cc. of sodium chloride solution.

Then, as 1000 cc. of silver nitrate solution contains 5 gm. AgNO_3 ,

$$29.0 \text{ cc. } \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{5 \times 29}{1000} = 0.145 \text{ gm. } \text{AgNO}_3.$$

Reference must be made to the reacting weights of the reagents with which we are concerned, namely, silver nitrate and chlorine; since standard solutions themselves do not contain this information it must be obtained from the reaction equation:



$$107.88 + 58.46 = 143.32 \quad \text{AgNO}_3 = 35.46 \text{ Cl.}$$

i.e. if 169.89 gm. of AgNO_3 reacts with 35.46 gm. Cl,

$$\therefore \quad 0.145 \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{35.46 \times 0.145}{169.89} = 0.0303 \text{ gm. chlorine.}$$

This amount of chlorine must be contained in the volume of sodium

chloride solution used—namely, 25 cc.—which has been found to react with the original volume of silver nitrate (29.0 cc., containing 0.145 gm. AgNO_3).

i.e. 25 cc. sodium chloride solution contains 0.0303 gm. chlorine.

1 " " " " " 0.0012 " "

(2) With Normal Solutions.

In a given solution of sulphuric acid it is required to determine the weight of acid per cubic centimetre.

The solution is titrated with normal sodium hydroxide. 35.0 cc. of normal sodium hydroxide is required to neutralise 25 cc. of the sulphuric acid solution. Reference can now be made to the reacting weights of the reagents by the fact that *all normal solutions are equal by volume*, and contain the equivalent of the reacting radicals in grammes per litre. Thus 35.0 cc. of normal sodium hydroxide = 35.0 cc. of normal sulphuric acid.

Normal sulphuric acid contains the equivalent of the reacting radical in grammes per litre, namely, 1.008 gm. hydrogen or 49 gm. of sulphuric acid per litre; e.g.,

1 cc. normal sulphuric acid contains 0.049 gm. sulphuric acid.

35.0 cc. " " " " $0.049 \times 35 \text{ gm.} = 1.715 \text{ gm.}$

\therefore 25 cc. examined " " " " 1.715 gm. " "

and 1 cc. " " " " 0.0686 gm. " "

COLORIMETRIC ANALYSES

In colorimetric analyses use is made of the intensity of colour which a solution gives with some reagent. This colour intensity is matched by adding a standard solution of the substance to the same amount of reagent, or by diluting a solution of a definite amount of the substance and reagent; the amount of substance required to produce the same depth of colour gives the concentration of the examined solution. Typical examples include the estimation of ammonia by means of Nessler reagent, and the estimation of nitrites in which use is made of the intense azo colours formed with aromatic amines. Stock standard colour solutions are prepared simultaneously, as these delicate tints are liable to change.

Various weight, measure, and temperature scales are in use in this country, and differences of choice exist between the medical and analytical professions. For the sake of uniformity the centimetre-gramme system is adhered to throughout the work, and conversion tables are given in the Appendix.

AIR

AIR is a mixture of oxygen, nitrogen, inert gases, carbon dioxide, and aqueous vapour, with traces of ammonia, nitrous and nitric acids, and hydrogen. At sea-level it exerts an average pressure of about 15 lb. per square inch, supporting a column of mercury 760 mm. high. The density of the atmosphere varies with height and at 18,000 feet it is only half that of the density at sea-level. It can be shown that air is a mixture by mechanical separation of its constituents, as, for example, by diffusion, partial solution, and fractional distillation. It can also be prepared by simple mixture of the constituents in the required percentage proportions. The average composition (dry) is :

	Per Cent. by Volume.
Oxygen	20.93
Nitrogen	78.07
Inert gases	0.94
Carbon dioxide	0.03
Aqueous vapour	variable

The composition of air at various heights and parts of the atmosphere is remarkably constant, and its oxygen content may be regarded as fixed unless the air is charged with abnormal quantities of foreign gases.

In insufficiently ventilated rooms occupied by large numbers of people, air becomes vitiated and causes discomfort to the inhabitants. It has been definitely established that a greater amount of disease and a higher death-rate are associated with insufficiently ventilated atmospheres. The various properties of vitiated air are usually attributed to diminution of oxygen, to excess of carbon dioxide produced by respiration, and to the presence of a supposed organic poison. Professor Hill and his collaborators have made the question the subject of a very thorough investigation. They concluded that, even in overcrowded spaces, oxygen is seldom diminished by 1 per

cent. owing to respiration, that carbon dioxide may be increased artificially to an extent beyond that prevailing in the most vitiated air without producing discomfort, and that respired air contains no poison.¹ They showed that the deleterious action of vitiated air is occasioned by rise in temperature, excessive water vapour, and lack of movement causing heat stagnation.

The quantities of carbon dioxide, aqueous vapour, and suspended matter in the air are usually regarded as indicative of its suitability for consumption.

Carbon dioxide, in addition to its normal presence in air, is produced by respiration, by combustion, and by plants, therefore the amount is liable to considerable variation. In open spaces under normal conditions it varies from 2.5 to 4.0 parts per 10,000. This amount increases in the absence of means for the rapid diffusion of carbon dioxide produced extraneously, as, for instance, in large towns and ill-ventilated crowded rooms. Excessive carbon dioxide collects in the neighbourhood of lime-kilns, in mines, and in rooms where stoves, lamps, or gases are burning. Carbon dioxide is not poisonous, and may be increased to as much as 200 parts per 10,000 without causing discomfort in breathing; in the presence of organic impurities, aqueous vapour, and dust, its increase by respiration to 12 parts per 10,000 renders the air unhygienic. This amount may be accepted as the sanitary limit.

The amount of aqueous vapour in air varies with the proximity to the sea, with seasonal and meteorological conditions, and with its production by respiration and combustion. The concentration of aqueous vapour cannot rise above a maximum, which increases with temperature; at maximum concentration the air is said to be saturated. The amount necessary for saturation (expressed in grammes per cubic metre) is termed the *maximum humidity*. The amount actually present (expressed the same way) is the *absolute humidity*, and the percentage proportion of the absolute to the maximum is the *relative humidity*. The *dew-point* is the temperature at which the absolute would become the maximum humidity. When the temperature of air saturated with aqueous vapour falls, the maximum concentration also falls, and the excess of

¹ *Local Government Board Reports, New Series, 100, 1914.*

aqueous vapour is precipitated as cloud, fog, rain, etc. In this country the aqueous vapour nearly always approximates saturation. An atmosphere saturated with aqueous vapour retards the normal evaporation of perspiration and is very oppressive. Excessive humidity of air greatly increases the noxious activity of its impurities and renders extremes of cold and heat more difficult to bear; dry air is also considered objectionable. A relative humidity of 73 to 75 per cent. is regarded as hygienic.

Air is occasionally charged with particular impurities, many of which are offensive or poisonous. Of these may be mentioned leakage from gas-pipes, fumes from factories, products of incomplete combustion, and effluvia from drains and fields. Illuminating gas contains large quantities of carbon monoxide, which is fatal when present in the air to more than 0.5 per cent.; carbon monoxide is also introduced by incomplete combustion in open fires or stoves, especially when charcoal is burned. Complete combustion converts it into the non-poisonous carbon dioxide. The compounds of sulphur contained in illuminating gas give acid fumes on combustion, and are restricted; according to the Metropolitan Gas Referees' standard, for instance, sulphuretted hydrogen must be absent, and the sulphur in other compounds must not exceed 17 grains per 100 cubic feet. Poisonous and irritating gases are evolved by certain manufactories; these are variously designated as trade nuisances and, where it has not been found practicable to eliminate them, they come under the control of the Board of Trade regulations. Effluvia from drains, stagnant water, and decomposing material can be detected in air, in addition to their odour, by the presence of excess of carbon dioxide, of free and albuminoid ammonia, and sulphuretted hydrogen.

In the analysis of air undertaken as tests of the sanitary condition of living spaces the estimation of oxygen is not necessary, but in exceptional cases it may be desirable.

An excess of carbon dioxide is accepted as an indication of the amount of respiratory impurity in air in the absence of other sources. Injurious gases, including carbon monoxide, sulphur dioxide, chlorine, and hydrochloric acid, seldom require quantitative estimation. The desiderata for a hygienic condition of air may be summarised as :

Temperature, 15.5°C. to 16.5°C.

Carbon dioxide not exceeding 12 parts per 10,000.

Difference of wet and dry bulbs, 4 to 8°F. (2 to 4.5°C.).

Relative humidity, 73 to 75 per cent.

Absence of injurious gases.

COLLECTION OF AIR SAMPLES

It is important that the bottles for collection of air samples be thoroughly clean, and, except for the first method of sampling described below, quite dry. To ensure perfect tightness, stoppers are thinly smeared with vaseline, or tight-fitting corks are previously immersed in paraffin wax of high melting-point.

Many methods are employed for the collection of samples. Perhaps the most simple is to fill completely the container with good tap water, and to empty it where the sample is to be taken; the air occupies the space of the water poured out. This method is useless where quantitative volumetric determinations are required, owing to partial or complete solution of constituents in the water. Another method without this disadvantage is to connect a tube reaching to the bottom of the sample bottle with an aspirator, and to draw through a volume of air at least six times the capacity of the bottle; or the sample may be obtained by blowing through the bottle with an ordinary hand bellows. Where only a small sample is required the aspiration can be done by mouth, as described with the Haldane apparatus (page 21). In cases where a sample is being taken for the determination of carbon dioxide as an index of the efficiency of ventilation, the following particulars should be supplied:

- (1) Place of collection.
- (2) Date and hour of collection.
- (3) Ventilation actually in use at the time.
- (4) Cubic space per person occupying the compartment.
- (5) Wet and dry bulb temperature readings in the compartment.
- (6) Wet and dry bulb temperature readings in the open air.
- (7) Any other information of interest.

CARBON DIOXIDE

Three methods for the estimation of carbon dioxide in air are in common use—those of Haldane, Pettenkoffer, and Lunge-Zeckendorf. Of these, Haldane's method stands apart as being in every respect superior. It is the most convenient to use,

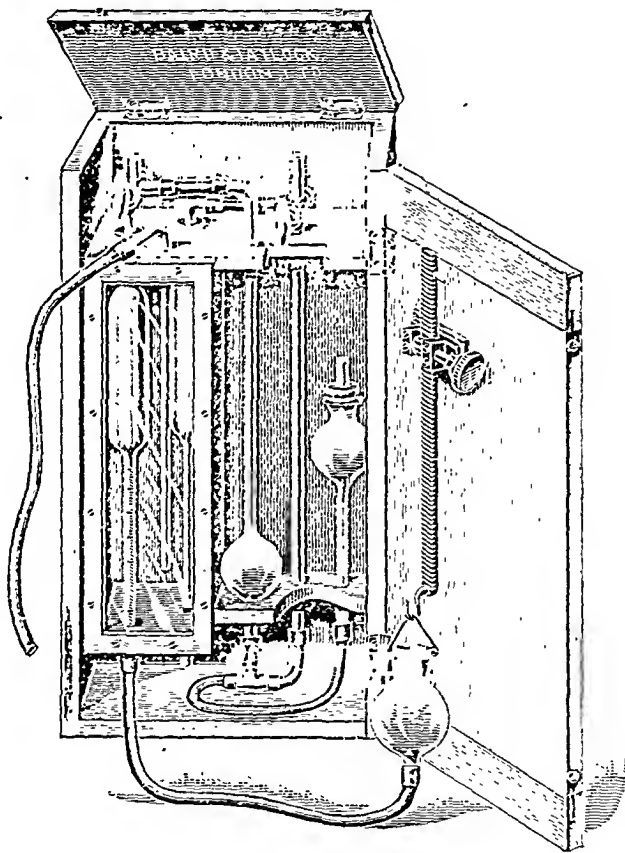


Fig. 3.

gives accurate results in a minimum of time, and requires very small samples. Results are obtained in three minutes when the air is drawn direct into the apparatus (Fig. 3), and seven minutes suffices for the examination of air from the sample bottle. The small volume of the sample necessary, about 20 cc., is a great advantage in considering the question of transport. The Haldane apparatus yields nothing in accuracy to the Pettenkoffer method, which, moreover, requires at least 5000 cc. of

sample, and occupies more than an hour of time. On account of the ordinary apparatus employed, the Pettenkoffer process still finds occasional use. The Lunge-Zeckendorf method is of little value except where large quantities of carbon dioxide are present, and is useless with air containing free acid.

HALDANE'S APPARATUS¹

The principle is that the carbon dioxide of the air sample is absorbed by caustic potash and the consequent diminution in volume, measured on the graduated scale, gives a direct reading of the quantity of carbon dioxide present in 10,000 parts of air. A trace of dilute sulphuric acid must always be present in the burette to keep the air therein saturated with moisture, the same purpose being achieved in the control tube by keeping the stem full. The potash solution should be about 10 per cent. strength, and it is preferable to colour it with methyl orange; movements of the liquid are thereby made more apparent. A more definite meniscus is obtained if a small sheet of some black material is placed behind the marks on the tubes R and S (Fig. 4). A blowing bulb may be used to provide the air current for agitating the water in the water jacket, instead of blowing by the mouth; the water jacket should be full to about half an inch from the top. The glass tubes and air burette must be perfectly clean, and thin pipe cleaners which can pass through the stopcocks serve admirably for dislodging any dirt.

The air to be examined may be taken either direct into the apparatus and tested at once, or can be drawn into suitable small bottles and despatched where necessary for examination. In the former case the examination of the sample only requires the use of the apparatus itself, but in the latter, accessories are needed.

The following is the procedure employed when the air to be tested is taken direct into the apparatus. Having placed it where the sample has to be taken, the tap A (Fig. 4) is turned to allow free communication between the air burette, the

¹ *The Estimation of Carbon Dioxide in Air by Haldane's Apparatus*, by Robert C. Frederick, reprinted from the *Journal of the Society of Chemical Industry*, January 31, 1916.

absorption bulb F, and outside, and similarly the tap B to allow communication between the control tube E, the tube S, and outside. By raising the potash reservoir H, the potash level is adjusted to the mark on S; the mercury in the graduated stem of the air burette is adjusted to about zero by the rack-and-pinion arrangement L. The tap A is now turned to establish communication with the outside only, and then the mercury reservoir is taken off the hook at L and raised in the hand until the mercury completely fills the air burette. On

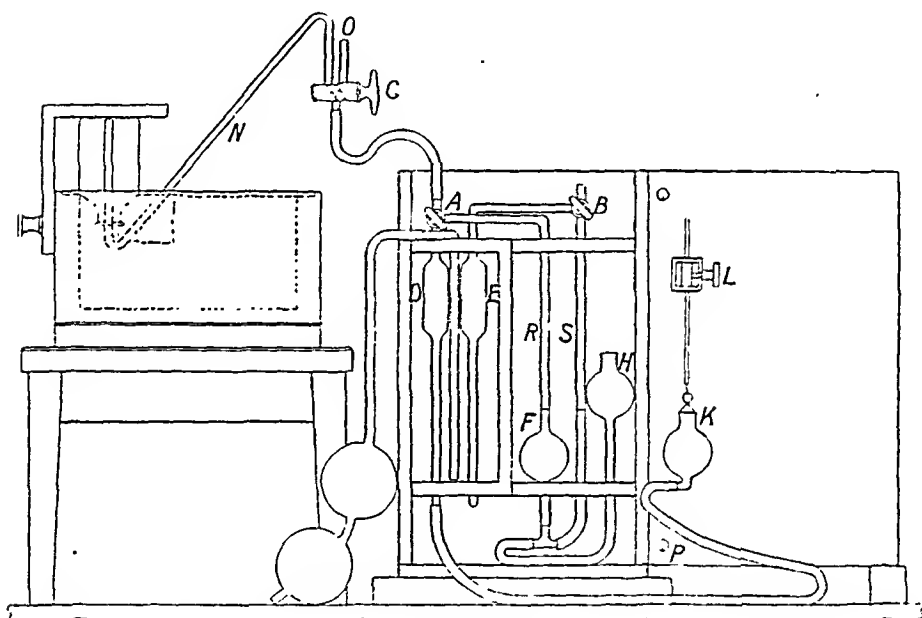


Fig. 4.

replacing the reservoir on the hook, the sample is drawn in, and the mercury falls to its former mark near zero. Some mercury is almost invariably caught in the stopcock, and must be removed by turning tap A into the position that the air burette and the absorption bulb only are in communication and then squeezing sharply, at the point nearest the stopcock, the rubber tube connecting them. The mercury globule drops into the graduated stem of D, and is made to unite with the mercury of the reservoir by giving A an eighth turn, thus closing all communication, and then gently raising K in the hand; the reservoir is replaced on the hook at L. The trouble with the

mercury globule can be obviated by using a stopcock, A, of the pattern having two parallel channels, suggested by Butterfield, but this necessitates the introduction of a third stopcock at the top of the tube R. The apparatus is now placed on a table or bench out of draughts and in a good light. The tap A is now again turned to place the air burette in communication with the absorption bulb only; similarly B is turned to place the control tube in communication with the tube S only. If the potash level at S has altered, it is corrected by raising or lowering the potash reservoir and then, by raising or lowering the mercury reservoir with the rack-and-pinion arrangement, the potash level is adjusted to the mark on R. The rubber tubing connecting F and H must be sharply squeezed to make sure that the potash levels return to their marks; if they do not, further adjustment is necessary. During the time these adjustments are being made by the right hand, the left is engaged in gently blowing air through the water jacket by squeezing the blowing bulb. The potash levels being correct, the mercury level is read on the graduated scale and noted. The carbon dioxide contained in the air is now absorbed. The air is made to pass over to the potash in the absorption bulb by taking the mercury reservoir in the right hand and slowly raising it until the mercury almost reaches the stopcock A, the left hand meanwhile giving an occasional squeeze to the blowing bulb. This operation is repeated four times, the mercury in each case being allowed to fall somewhere in the graduated stem. The mercury reservoir is replaced on the hook at L. With a steady flow of air being maintained through the water jacket, the potash levels are adjusted to the marks on R and S as already described, the same precautions as to nipping the rubber tubing connecting F and H being taken. The mercury level in D is again read, and this figure, less the first, gives a direct reading of the quantity of carbon dioxide present per 10,000 parts of air. For example, if the first figure was 2.2 and the second 7.8, the result is $(7.8 - 2.2) = 5.6$ parts per 10,000. When the test is finished, the taps A and B are turned to close communication in all directions, otherwise the potash may rise in the tubes and cause trouble.

When taking samples of air in bottles for subsequent testing by Haldane's apparatus, the bottles used are 2 oz. narrow-mouthed, squat form, and closed with ground stoppers smeared with a thin coat of vaseline. They must be perfectly clean and dry. To prevent the stopper coming out, particularly when the bottles are exposed to changes of temperature and pressure, a broad rubber band is placed over it and under the bottle; another smaller band is doubled over this round the neck to keep the first one in position.

The air sample is collected in the following manner. One end of a rubber tube ($\frac{3}{16}$ in. bore and about $2\frac{1}{2}$ ft. long) is introduced into the bottle until it rests on the bottom, the other end being held in the mouth; the air is then sucked through, and the tube removed while the final air is still being sucked up. It need hardly be emphasised that breath must not be allowed to pass backwards into the bottle, and it is also important that the bottle should be held at arm's length to prevent contamination of the air in the immediate vicinity of the bottle. The stopper is inserted, turned round, and secured with the rubber bands.

The extraction of the air from these sample bottles requires the use of a mercury bath, and a bent glass tube N, of narrow bore, fitted with a three-way stopcock C, of the pattern illustrated. The glass tube is attached to the stopcock A of the Haldane apparatus by rubber tubing. The mercury bath is made of wood and has a narrow slit $\frac{5}{16}$ in. wide, $3\frac{3}{4}$ in. deep, and 6 in. long, which broadens out, at the end in which the bottle is opened, to a rectangular space, $2\frac{7}{8}$ in. long, $1\frac{1}{2}$ in. wide, and $1\frac{1}{2}$ in. deep. Butterfield has suggested the useful clamp shown, and also the provision of a raised flange about $\frac{1}{16}$ in. high, which prevents the overflow of mercury during the process of removing the stopper of the bottle. A lid which fills the depression caused by this flange prevents the access of dust whilst the bath is not in use. It is necessary that the bath be raised, and the little table shown has been made for the purpose. It is $7\frac{1}{2}$ in. high, and the top, $9\frac{1}{2}$ in. long and $7\frac{1}{2}$ in. broad, has a rim $\frac{3}{4}$ in. high round it, which prevents any loss of mercury. The arrangement of the

complete apparatus is shown in Fig. 4. The Haldane apparatus itself rests on a block of wood inside a dish, which serves to catch any water that may overflow when the water in the water jacket is being agitated. The bottle is placed neck first into the mercury, the stopper removed by two fingers, and the bottle clamped rigid. The taps A and B of the Haldane apparatus are turned to allow free communication throughout in the manner described. The potash is then adjusted to the mark at S, and the tap A turned to establish communication between the air burette and the outside only; the mercury should read about 7 on the graduated scale of D. The rubber tubing fastened to the stopcock C, the latter being open to the bent tube N, is attached to the stopcock A. Holding the glass tube in the left hand, over the mercury bath, the mercury reservoir is taken from the hook at L and raised in the right hand until the mercury completely fills the air burette, the rubber connection, and the glass tube. Still holding the mercury reservoir above the level of the bent tube N, the tap C is turned to close communication in all directions; the tap A is similarly treated by giving an eighth turn. The tube N is now pushed through the mercury in the bath into the sample bottle and the mercury reservoir attached to the hook P. Stopcock C is opened to A and N, and A to the air burette only. The mercury now returns to the reservoir, and air from the sample bottle is drawn into the Haldane apparatus. When D becomes about half full of air, the rubber tube between A and C is closed by firmly pressing with two fingers, and when the mercury has quite stopped flowing, the fingers are suddenly withdrawn and the mercury allowed to continue running. This last operation is necessary to dislodge the mercury which frequently remains in the rubber connection. In a few seconds the mercury comes to rest, and the taps C and A are again turned to close communication in all directions. More air has been extracted than is required for the test, and the excess is blown off by placing K on the hook at L, opening A to C and the latter to O. The tap A is turned to establish communication between the air burette and the absorption bulb only, and similarly B to place the control tube in communication with the tube S only. From this stage the manipulation is

the same as described in the account of the procedure employed when the apparatus alone is used, and the same point, namely, the admission of the air in the Haldane apparatus, has been reached. The mercury globule is removed, the potash levels are adjusted, the carbon dioxide is absorbed, and the levels are readjusted as before, the same attention to detail being given.

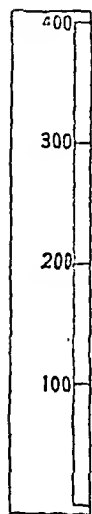


Fig. 5.

With the ordinary small Haldane apparatus, readings to 100 parts per 10,000 can be obtained. In the great majority of cases this is quite sufficient, but it sometimes occurs that the amount of carbon dioxide is much above this figure, and the following is an account of Frederick's simple device for making the apparatus record up to 500 parts per 10,000.

First, it is necessary to measure with absolute accuracy the distance the potash level rises in the glass tube R (Fig. 4), when the mercury is brought from 100 to 0 on the air

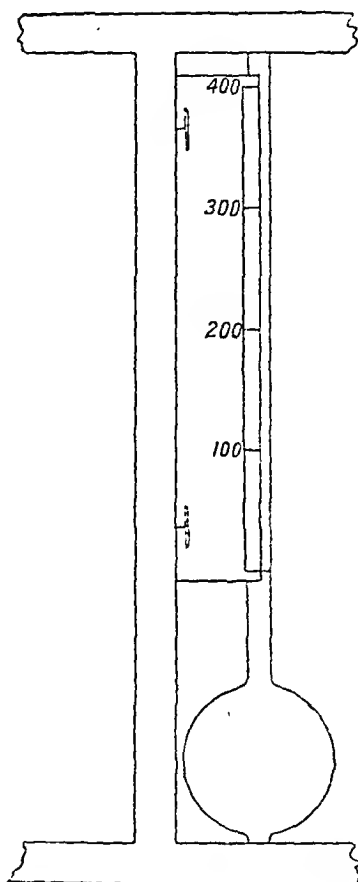


Fig. 6.

burette scale, the level in S being kept at the mark. It is understood that the air is enclosed, as it would be if ready for absorption of carbon dioxide. A stiff piece of cardboard is now marked down one side with four divisions, each being exactly this distance found; the other side is bent at right angles. The result is a scale as shown in Fig. 5. This is pinned with drawing pins to the outside of the water jacket, as shown in Fig. 6, the zero coinciding with the mark on R (Fig. 4), and the edge of the scale running down the centre of the tube. When in

use the potash level is adjusted in the usual way, after absorption of carbon dioxide, to the nearest hundred mark, and the reading on the air burette scale is also taken. If the mercury reservoir has been raised, the result is obtained by adding the increase on the air burette scale to the reading on the cardboard scale, and similarly, if the mercury reservoir has been lowered, by subtracting the decrease on the air burette scale. Two examples will make this clear.

EXAMPLE 1 :

Before absorption. Air burette scale, 6.4.
 After " " " " 77.8. Card-
 board scale, 200.
 $(77.8 - 6.4) + 200 = 271.4$ parts CO_2 per 10,000.

EXAMPLE 2 :

Before absorption. Air burette scale, 8.6.
 After " " " " 2.8. Card-
 board scale, 300.
 $300 - (8.6 - 2.8) = 294.2$ parts CO_2 per 10,000.

Such a cardboard scale is, of course, only meant for occasional use ; a permanent arrangement can be obtained by having the tube R itself (Fig. 4) graduated as shown in Fig. 7.

The apparatus shown in Fig. 8 (Frederick) is a useful adjunct to the Haldane apparatus when used for testing samples in the laboratory. If a large number of tests have to be done, the physical effort required to lift the mercury reservoir becomes a serious consideration. The apparatus is $19\frac{3}{4}$ in. high, and the size of the parts can be judged from this. It is large enough to work with the more modern form of the Haldane apparatus, which is contained in a larger case than the older pattern. A is a boxwood cage or nest into which the mercury reservoir can easily be placed and as easily removed. It is connected by a cord, over pulleys, to a brass lead shot container B, which slides up and down the rod C; this container balances the mercury reservoir. In use, the reservoir,

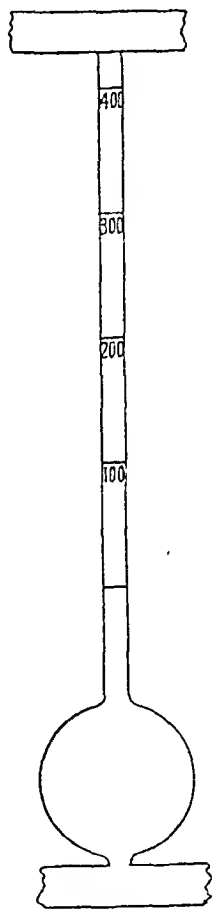


Fig. 7.

after the first reading has been taken, is placed in the cage and raised or lowered by moving B down or up C. The adjustable stops D compel the mercury to travel between any points desired, and prevent it rising too far and flowing into the potash or falling too low and drawing in the potash. The

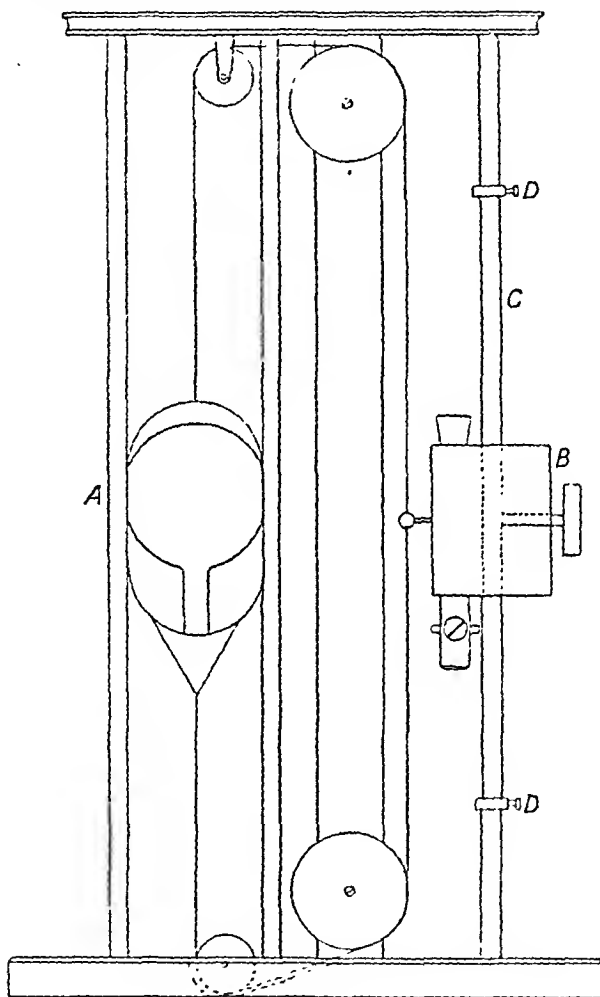


Fig. 8.

narrow bore of the air burette ensures that the mercury will not travel too quickly. When sufficient absorptions have been given, the mercury reservoir is taken from the cage, replaced on the hook of the rack-and-pinion arrangement, and the analysis completed in the ordinary way.

CLEANING OF MERCURY

To clean mercury for use in the Haldane apparatus, etc., it is

passed through the apparatus shown in Fig. 9. The soiled mercury is placed in B and passes through a capillary tube and falls in a fine jet through dilute nitric acid (one part concentrated with four parts of water). The clean and sufficiently dry mercury collects in C. Before using the apparatus a small quantity of clean mercury is placed in A and D.

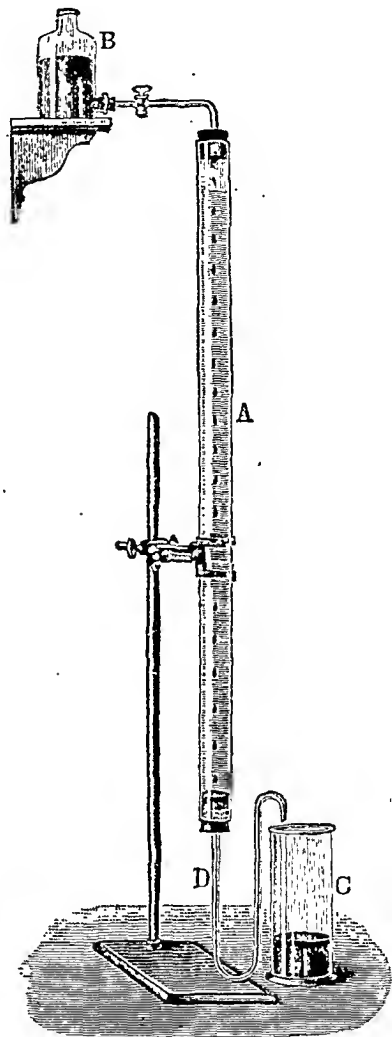
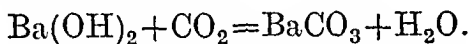


Fig. 9.

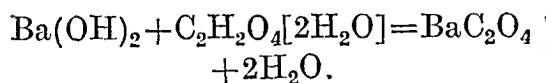
PETTENKOFFER'S METHOD

The principle of this process is that the carbon dioxide is absorbed by barium hydroxide, and the amount is determined by the loss of alkalinity in the absorbing medium.

Barium hydroxide is neutralised by absorption of carbon dioxide with the formation of barium carbonate.



Barium hydroxide is also neutralised by oxalic acid, with the formation of barium oxalate.



From these equations it is seen that one molecule of carbon dioxide has the neutralising power of one molecule of oxalic acid, and therefore 44 gm. of carbon dioxide is equivalent to 126.06 gm. of crystallised oxalic acid. Now the molecular weight in gm. of all gases occupies 22.33 litres at N.T.P. (*g.v.*); therefore 126.06 gm. of crystallised oxalic acid is equivalent to 22.33 litres of carbon dioxide, and 5.6453 gm. of oxalic acid to 1 litre of carbon dioxide. Hence 1 cc. of a solution containing 5.6453 gm. of crystallised oxalic acid in 1 litre is equivalent to 1 cc. of carbon dioxide.

Solutions required:

Standard oxalic acid solution.

The above oxalic acid solution is diluted 1 in 5, 1 cc.=0.2 cc. CO₂. Oxalic acid does not decompose the barium carbonate formed in the process.

Barium Hydroxide Solution.

3.5 gm. of barium hydroxide is dissolved in water with about 0.2 gm. of barium chloride, and made to 1 litre; the barium chloride is added to convert any sodium or potassium hydroxide present as impurity into the barium salt.

The solution is stored in a special form of bottle fitted with a two-holed cork. Through one hole passes a syphon tube reaching almost to the bottom, and having a piece of rubber tubing with a pinch-clip at the exit; through the other passes a right-angle tube connected to a small U tube containing pieces of potassium hydroxide, by which the carbon dioxide of the incoming air is absorbed.

Phenolphthalein.

1 per cent. in absolute alcohol.

Process:

The sample is collected in a wide-mouthed bottle of about 8000 cc. known capacity, with a tight-fitting cork containing two holes closed with pieces of glass rod.

50 cc. of barium hydroxide solution is measured in a pipette by placing the tip into the projecting rubber tube of the stock bottle exit and opening the clip. This is transferred to the sample bottle by removing one of the glass rods of the cork, and immediately placing the pipette through the hole; the other rod is removed and the solution run in. One cc. of phenolphthalein is also added from a pipette, and the glass rods are replaced. The bottle is laid on its side and occasionally rolled and shaken, care being taken to prevent the liquid touching the cork. If the liquid does not remain distinctly pink, the barium hydroxide has been neutralised, and a further 50 cc. is added.

Meanwhile the barium hydroxide solution is standardised with the oxalic acid. 25 cc. is removed from the stock bottle as already described and transferred to a small flask having a long narrow neck. With about 1 cc. of phenolphthalein as indicator, the solution is titrated with standard oxalic acid from a long-nosed burette, until the pink colour is discharged. It is important that outside air should be excluded as far as possible. The quantity of oxalic acid required is noted.

At the expiration of an hour one rod is removed from the cork of the sample bottle, the nose of the burette containing oxalic acid passed through, and the liquid titrated direct into the sample bottle. From the data obtained the quantity of carbon dioxide present in the sample is calculated. The temperature and pressure of the air in the space examined are noted at the commencement of the experiment.

EXAMPLE :

Capacity of the sample bottle, 8195 cc.

Volume of sample examined = 8195 less 50 cc. of barium hydroxide and 1 cc. of phenolphthalein = 8144 cc. at 16° C. and 749 mm. pressure.

25 cc. of barium hydroxide originally equalled 23.9 cc. standard oxalic acid.

∴ 50 cc. of barium hydroxide originally equalled 47.8 cc. standard oxalic acid.

After absorption of carbon dioxide in sample bottle,

50 cc. of the barium hydroxide solution = 22.4 cc. standard oxalic acid.

∴ carbon dioxide absorbed is equivalent to $47.8 - 22.4 = 25.4$ cc. standard oxalic acid.

Now 1 cc. standard oxalic acid = 0.2 cc. of carbon dioxide.

∴ 25.4 " " " = 5.08 cc. of carbon dioxide at N.T.P.;
i.e. there is 5.08 cc. of carbon dioxide in the volume of air taken.

The volume of the sample taken is corrected to normal temperature, 0° C., and pressure, 760 mm. (N.T.P.). The volume of all gases at constant pressure increases $\frac{1}{273}$ of their volume for each degree C. rise in temperature above -273° C. (absolute zero), and at constant temperature varies inversely as the pressure. Therefore the volume of a gas at normal temperature and pressure is proportional to its recorded volume as 273 is to the absolute temperature ($273 + ^\circ\text{C.}$), and as the pressure of the gas is to 760 mm.

From these facts, then, the volume of a gas at N.T.P. can be calculated from the general formula,

Volume at N.T.P. =

$$\text{Recorded volume} \times \frac{273}{\text{Absolute temp. in degs. C.}} \times \frac{\text{Pressure in mm.}}{760}$$

Therefore in this example the corrected volume = $8144 \times \frac{273}{280} \times \frac{740}{760} = 7582$ cc.

Therefore there is 5.08 cc. of carbon dioxide in 7582 cc. of the sample = 6.70 parts per 10,000.

LUNGE-ZECKENDORF METHOD

Lunge and Zeckendorf's method is occasionally useful where only an approximate estimation is necessary and the quantity of carbon dioxide present is considerable.

The apparatus, which is used direct in the space to be tested, is shown in Fig. 10. The method depends on the conversion of

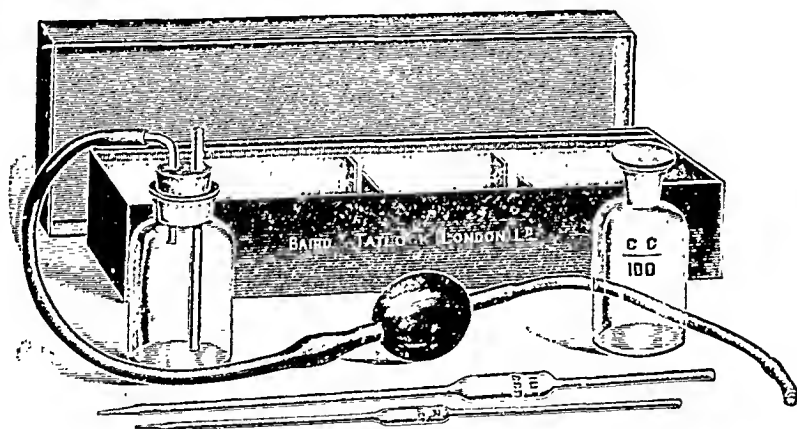


Fig. 10.

a dilute solution of sodium carbonate to bicarbonate by the carbon dioxide of the air; the completion of the process is indicated by the discharge of the colour given with phenolphthalein.

Solution required:

2.65 gm. of pure and dry sodium carbonate and 0.05 gm. of phenolphthalein are dissolved in water and made to 500 cc.

Method:

2 cc. of the above stock solution is pipetted into the graduated stoppered bottle and made to 100 cc. with recently boiled cold

water. This dilute solution is only satisfactory for the day on which it is prepared. 10 cc. is transferred with a pipette to the bottle of the apparatus and the cork is firmly replaced. Contamination of the air with the breath in the immediate vicinity must be avoided. The rubber blowing ball is attached to the longer glass tube, taken between the palms of the hands, and gently and completely compressed. By this means a definite volume of air (70 cc.) is pumped through the solution. The bulb, which is fitted with a special valve, is allowed to refill by releasing the hands, and the bottle is well shaken. This process is repeated until the pink colour is discharged. From the following table, calculated by the originators of the test, the quantity of carbon dioxide present is found from the number of compressions required.

LUNGE-ZECKENDORF TABLE

Compressions.	CO ₂ per 10,000.	Compressions.	CO ₂ per 10,000.
2	30.0	16	7.1
3	25.0	17	6.9
4	21.0	18	6.6
5	18.0	19	6.4
6	15.5	20	6.2
7	13.5	22	5.8
8	11.5	24	5.4
9	10.0	26	5.1
10	9.0	28	4.9
11	8.7	30	4.8
12	8.3	35	4.2
13	8.0	40	3.8
14	7.7	48	3.0
15	7.4		

THE HALDANE APPARATUS FOR GENERAL AIR ANALYSIS

The Haldane apparatus shown in Fig. 11 is the most suitable for general air analysis. When the necessary dexterity has been acquired by practice, accurate determinations are

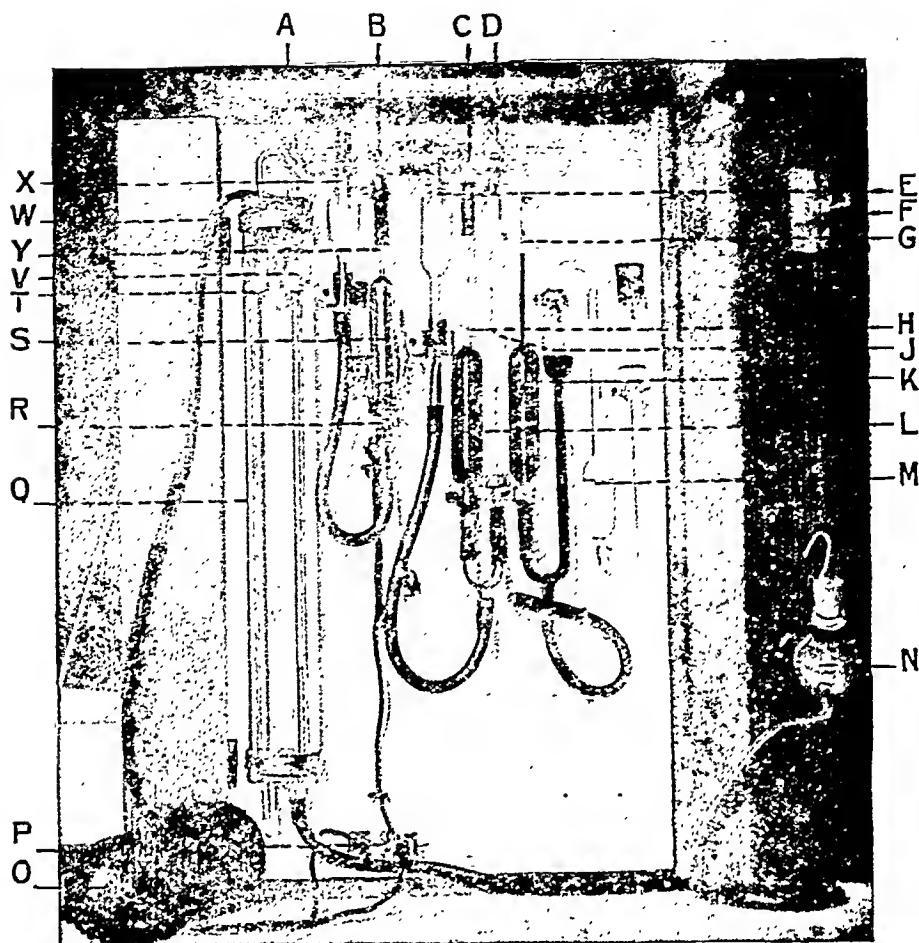


Fig. 11.

HALDANE'S GENERAL AIR ANALYSIS APPARATUS

- | | |
|---|------------------------------------|
| A. Stopcock of burette. | B. Stopcock of combustion chamber. |
| C. Stopcock of potash and pyrogallol absorption bulb. | |
| D. Stopcock of control tube. | E. Potash reservoir. |
| F. Rack-and-pinion adjusting arrangement. | |
| G. Mark on pyrogallol bulb. | H. Mark on potash bulb. |
| J. Mark on potash tube connected to control tube. | |
| K. Pyrogallol absorption bulb. | L. Potash absorption bulb. |
| M. Potash sealing tube. (Sealing pyrogallol absorption bulb.) | |
| N. Mercury reservoir. | O. Blowing ball. |
| P. Terminals from combustion chamber. | Q. Water jacket. |
| R. Terminals of combustion chamber. | S. Combustion chamber. |
| T. Control tube. | V. Air-measuring burette. |
| W. Tube from blowing bulb through water jacket. | |
| X. Mercury reservoir for combustion chamber. | |
| Y. Mark on combustion chamber. | |

rapidly made. The whole is portable and is contained in a case measuring $11\frac{3}{4}$ in. \times $20\frac{1}{2}$ in. \times 3 in. ; for combustion processes a small combined battery and rheostat is also required. In general principle the apparatus is similar to that designed for the estimation of carbon dioxide only, and it can be used either directly in the air to be examined or for testing samples at the laboratory. In the latter case the sample bottles and accessories already described, (page 24) are used.

Description of the Apparatus

3 cc. of the air-measuring burette V is graduated to 0.01 cc. on the narrow stem, and opens into a bulb graduated in cc. only, the total capacity being 10 cc. Through the stopcock A the burette can be opened to the outside or towards stopcocks B and C. B is attached to the combustion chamber S; this is full of mercury, which can be displaced into the reservoir X, exposing a platinum spiral for combustion purposes. The spiral is made red-hot by connecting the terminals R with a 4-volt battery or accumulator with rheostat; it is much more convenient to solder a twin lead to these terminals and attach to brass screw terminals P, fixed in the bottom of the case. Stopcock C is on the potash absorption bulb L, and also controls the pyrogallol absorption bulb K. A plain control tube T, of about equal capacity to that of the air-measuring burette, acts through stopcock D on the other limb (with mark J) of the potash absorption section; for this reason all measurements are made between the mercury from N and the potash solution in L. It is an advantage to attach a larger mercury reservoir N than that supplied on the apparatus. The air burette and control tube are contained in a water jacket Q to give uniformity of temperature, and the water in this is mixed by squeezing the blowing ball O attached to the tube W which passes to the bottom of Q. The blowing ball is not supplied with the apparatus, the intention being that the mixing can be done by the mouth. The mercury in the air burette is adjusted by the rack-and-pinion arrangement F.

Each stopcock is three-way; a channel passes right through in one direction, and another channel proceeds from the centre

of this at right angles at one side only. The position of this short channel is indicated by a black spot on the stopper.

Differences in volume due to absorption and combustion are measured on the graduated scale of the air burette, and are calculated to percentage or parts per 10,000.

Preparation of the Apparatus

With A open to the outside, the reservoir N is filled with mercury. A trace of dilute sulphuric acid is placed in both the air burette and the control tube. In the latter it can be introduced at the open end, with D open towards T and the outside only, and forced down by sharp blasts from a blowing bulb half closing the orifice. Mercury is also placed in the combustion chamber to about the mark Y through X with B open to A only, and A open to the outside. Ten per cent. potassium hydroxide solution, coloured with methyl orange, is introduced, through E, to the bulb L and tube from control tube (with mark J), with C open towards B only, the latter to A, and A to the outside; D is open to the outside. The potash is added to about the marks H and J. Pyrogallol solution is run into K through the rubber tube attached, which is then closed with a piece of glass rod. The pyrogallol solution recommended by Haldane is a nearly saturated solution of potassium hydroxide (sp. gr. 1.55), to each 100 cc. of which has been added 10 gm. of pyrogalllic acid. The solution should be prepared some time before use, and a rubber stopper used for the stock bottle. This method inevitably causes a considerable loss of absorption power in the pyrogallol solution owing to contact with atmospheric oxygen.* A better way is to make a suspension of 3 gm. pyrogalllic acid with 4 cc. of water and to introduce this into K first; the dish used is then washed out with saturated potassium hydroxide solution into K to about the mark. The rubber tube is sealed as in the foregoing. To preserve the absorbent in K from outside air, a seal is effected by adding strong potash solution with a pipette into the bent tube M; this potash solution is not to be confused with that in L, which is the only solution referred to in the following description.

A safety catch is easily provided for the toothed bar of F

by placing a wire in the extreme top hole and twisting it round. Corks, with a capillary tube passing through them, should be fixed in X, E, and M. It is an advantage to attach two hook screws beside F as shown. All connections, which should be of stout black tubing, must be wired.

For samples in suitable bottles the mercury bath already described (page 24) is used in conjunction with the apparatus; the mercury reservoir propelling apparatus (page 27) is of very great assistance.

Manipulation of the Apparatus

Carbon dioxide and oxygen are determined by absorption with potassium hydroxide in L, and by alkaline pyrogallol solution in K respectively; combustible gases by burning in S.

There is very little freedom of action with the apparatus, and special care must be taken in the various steps of an analysis.

It will be evident that the procedure varies according to the composition of the air to be tested. The descriptions which follow are of the processes employed when using the apparatus direct in the space to be examined; with sample bottles the transference of the sample to the apparatus is carried out as detailed for the smaller apparatus.

ESTIMATION OF CARBON DIOXIDE AND OXYGEN; NITROGEN (AND INERT GASES) BY DIFFERENCE

Preliminary

When oxygen is to be estimated it is first necessary to remove all free oxygen from the apparatus. When the test immediately follows such a determination this step will be unnecessary, but if the apparatus has stood for some time any free oxygen must be absorbed in the pyrogallol solution. A is turned to place the air burette V in communication towards B, B open towards A and C only, and C to place the pyrogallol absorption bulb K in communication towards A only; D is turned to allow communication only between the control tube T and tube with mark J. The air is now passed into K for absorption of oxygen (any carbon dioxide is also absorbed at the same time) by raising the mercury reservoir N until the mercury almost reaches the stopcock A; the air returns to the burette

on lowering N. This operation is repeated about twenty times, and the mercury reservoir is replaced on the rack-and-pinion arrangement F at such a height that the pyrogallol level is in the neighbourhood of the mark G. The flow of mercury is best regulated by pinching between the fingers the tube connecting V and N. A small quantity of the original air will be retained between C and the potash level in L, and between B and the mercury level in S; the oxygen in these must also be absorbed. For this purpose stopcock B is turned to place S open towards A only, and the residual air is passed over into S and returned to V; B is turned open towards A and C only. C is now turned to place V in communication with L only; the air is then passed over into L and again returned to V. The small quantity of oxygen is absorbed as before in two or three absorptions. The trace of oxygen remaining is removed by repeating these operations; N is replaced on F. The mercury level at Y is adjusted exactly to the mark by movement of X, with B open to A, S, and C; B is then turned open towards A and C only. The water in Q is mixed by squeezing the blowing bulb O, and the pyrogallol level is adjusted exactly to the mark G by movement of F carrying N. C is now turned to shut off K and place L only in communication towards A. D is opened to the outside, to T, and towards J; by raising or lowering the potash reservoir E the potash level is adjusted exactly to the mark J. D is turned to its former position (open from T towards J only), and remains thus throughout the test following. Similarly by movement of N the potash level is now adjusted exactly to the mark H. The tube connecting E and L must be sharply pinched between the fingers after all adjustments of the two potash levels; if they do not return exactly to the marks H and J further adjustment is necessary. A is now turned to allow V to be open to the outside only.

The mercury level in V is adjusted to about 9.98; the residue from the absorption is now expelled by raising N until the mercury begins to run out of the burette. N is replaced at its former place on F, and the mercury, by returning to the reservoir, draws in the sample. When the mercury has come to rest, A is turned to give communication from V towards B only. To remove the globule of mercury which very commonly

is retained in the stopcock A, B is now turned to open S towards A only; by gently pressing the two limbs of the rubber tube connecting S and X against each other, the globule is displaced and drops into V. B is turned open towards A, S, and C, the level at Y again adjusted exactly to the mark, and B turned open towards A and C only. A is now given an eighth turn downwards to close communication in all directions, and N raised so that the mercury flows as far as the graduated stem of V to take up any small globules which may have remained suspended on the sides. A is now given an eighth turn upwards to place V again in communication through B towards C only. The position now is that the sample in the air burette is in communication with the potash bulb only, the control tube in communication with the other limb of the potash arrangement only (tube with mark J), and the mercury and pyrogallol levels are exactly at the marks Y and G respectively. A steady and gentle flow of air from O is maintained through Q to keep the temperature uniform in the water jacket during the time the potash levels at H and J are adjusted exactly to the marks by raising or lowering N and E respectively. The reading on V is immediately taken. With the aid of a magnifying lens it is possible to read to the third place of decimals, *i.e.* to 0.001 cc.

Carbon Dioxide

The air is passed over into L for absorption of carbon dioxide and returned to V; this is repeated fifteen times. Any trace of carbon dioxide retained between B and the mercury level in S, in the displacement of the mercury globule after taking in the sample, is removed by passing the air into S and returning to V; B is turned open in all directions, the level at Y adjusted exactly, and B turned open towards A and C only. The air is again passed into L four times for absorption of carbon dioxide. The reservoir N is replaced on F, so that the potash level falls about the mark H; the water in Q is mixed whilst the levels at H and J are exactly adjusted as before. The reading in V is now taken. The decrease in volume gives the quantity of carbon dioxide present in the volume of sample taken for the test and is calculated to percentage.

Oxygen

C is turned open from A towards K only, and the oxygen is absorbed by passing the air over into K ten times, allowing it to remain about one minute on each occasion. Oxygen shut in between B and the mercury level in S, and between C and the potash level in L, is removed and absorbed as already described; the level at Y is adjusted before turning B again open from A towards C only. N is replaced on F so that the pyrogallol level falls about the mark G and, while mixing the water in Q, is adjusted exactly to it; C is then turned to allow communication A to L only. The potash levels are adjusted exactly to H and J while mixing the water in Q. The reading on V is now taken, and, as before, the decrease in volume gives the quantity of gas absorbed. •

Nitrogen (and Inert Gases)

When carbon dioxide and oxygen have been determined, nitrogen and inert gases can be obtained by difference if other gases are absent.

EXAMPLE :

Volume of air taken for test 9.981 cc.

„ „ after absorption of carbon dioxide 9.634 cc.

„ „ after absorption of oxygen . . . 8.131 cc.

Carbon dioxide = $9.981 - 9.634 = 0.347$ cc.

0.347 cc. in 9.981 cc. = $0.347 \times \frac{100}{9.981} = 3.48$ per cent.

Oxygen = $9.634 - 8.131 = 1.503$ cc.

= 1.503 cc. in 9.981 cc. = $1.503 \times \frac{100}{9.981} = 15.06$ per cent.

Nitrogen plus argon = $100 - (3.48 + 15.06) = 81.46$ per cent.

COMBUSTIBLE GASES

Amongst the combustible gases are included carbon monoxide (CO), methane (CH₄), acetylene (C₂H₂), ethane (C₂H₆), ethylene (C₂H₄), and hydrogen.

The nature and quantity of these gases present in air can be calculated, after combustion, from the alteration in volume and amounts of carbon dioxide and water formed in the reaction. Excess of oxygen must always be present, and should be

in sufficient quantity to prevent explosive combustion ; if these conditions do not exist in the sample it is diluted as described later.

Method :

As the pyrogallol bulb is not used, it is cut out by stop-cock C. All carbon dioxide, free in the apparatus, is first removed by absorption in L and the levels at Y, H, and J are then adjusted exactly to the marks. A is turned open from V to the outside only, the sample is taken in and the volume measured as before. Carbon dioxide is then determined by absorption in the usual way. B is turned open from A towards S only, and N raised to displace the mercury in S into X. Connection is made with the battery and sufficient current used to cause the platinum spiral in S to become red-hot, but not to assume a greater temperature, otherwise the spiral may fuse. By manipulation of N the air is passed backwards and forwards over the spiral fifteen times ; the mercury in S is displaced as fully as possible, and allowed to return to just below the supports of the spiral and short circuiting avoided. The current is disconnected and ten minutes is allowed for S to become cold. N is placed on F, so that the mercury level falls about Y, and B is opened towards A, S, and C. The level at Y is adjusted exactly by X, and B is then turned open towards A and C only. The water in Q is mixed, the levels at H and J adjusted, and the volume of residue ascertained. Any carbon dioxide produced by the combustion is now estimated by absorption in L. The small quantity of sample which, previous to combustion, was retained between B and the potash level in L, and has therefore escaped combustion, is combusted by passing the air into S, and repeating the combustion for about one-third the time used on the first occasion ; the carbon dioxide produced is estimated as before.

Six data are then available for calculating the results : volume of sample (1) taken for test ; (2) after absorption of carbon dioxide ; (3) after combustion ; (4) after absorption of carbon dioxide produced by combustion ; (5) after second combustion ; (6) after absorption of carbon dioxide produced by second combustion.

EXAMPLE :

Sample of air containing carbon dioxide, carbon monoxide, and hydrogen.

Volume of sample taken for test	9.976 cc.
„ „ after absorption of carbon dioxide	9.753 cc.
„ „ after combustion	9.607 cc.
„ „ after absorption of carbon dioxide produced by combustion	9.573 cc.
„ „ after second combustion	9.568 cc.
„ „ after absorption of carbon dioxide produced by second combustion	9.567 cc.

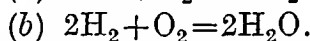
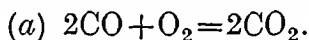
CARBON DIOXIDE

The carbon dioxide originally present and removed previous to the combustion = $9.976 - 9.753 = 0.223$ cc.

0.223 cc. carbon dioxide in 9.976 cc. sample
= 2.24 per cent.

COMBUSTIBLE GASES

The combustion in this case involves two equations :—



That is to say, (a) two volumes of carbon monoxide combine with one of oxygen to give two volumes of carbon dioxide, and the volume of carbon dioxide produced is equal to the volume of carbon monoxide originally present; the volume of oxygen which combines with the carbon monoxide is equal to half the volume of carbon dioxide produced by combustion. Similarly (b) two volumes of hydrogen combine with one of oxygen to give water (liquid), the proportionate volume of which is so small as to be entirely negligible; on combustion, therefore, the volume reduction is one and a half times the quantity of hydrogen present, or, in other words, the quantity of hydrogen present is two-thirds of the reduction in volume on combustion.

Now in this example the reduction in volume on combustion = $(9.753 - 9.607) + (9.573 - 9.568)$ cc. = 0.151 cc.

The total carbon dioxide produced by combustion = $(9.607 - 9.573) + (9.568 - 9.567)$ cc. = 0.035 cc.

CARBON MONOXIDE

The volume of carbon monoxide originally present is equal to the volume of carbon dioxide produced by combustion, = 0.035 cc. of carbon monoxide in 9.976 cc. sample = $0.035 \times \frac{100}{9.976} = 0.35$ per cent.

HYDROGEN.

The total reduction in volume on combustion is due to the union of both the hydrogen and the carbon monoxide with oxygen. Now the quantity of oxygen which has combined with the carbon monoxide is equal to half the volume of carbon dioxide produced, *i.e.* half of 0.035 cc.=0.0175 cc. The reduction in volume due to the union of oxygen and hydrogen only is therefore $0.151 - 0.0175 = 0.1335$ cc.; and two-thirds of this volume is the quantity of hydrogen present, *i.e.* $0.1335 \times \frac{2}{3} = 0.089$ cc., therefore hydrogen = 0.089 cc. in 9.976 cc. = $0.089 \times \frac{100}{9.976} = 0.89$ per cent.

The analytical results therefore read:

Carbon dioxide	2.24 per cent.
Carbon monoxide	0.35 „
Hydrogen	0.89 „

With other combustible gases, present singly or in mixtures, the calculation follows the same lines.

When dilution of the sample is necessary, pure air is taken into the apparatus and freed from carbon dioxide in the usual manner. The appropriate quantity of this is measured exactly and shunted into the potash bulb; A is turned to close communication in that direction with V open to the outside only, and a sufficient quantity of sample is then drawn in to make the total volume of sample and pure air just less than 10 cc. A is opened towards C, the pure air is added to the sample in V, and the total volume measured; the volume, minus the first reading, gives the quantity of sample taken for the test, which then proceeds in the ordinary way.

Estimation of Coal Gas

When an escape of coal gas has taken place in a space, it is sometimes required to determine the extent of its presence. This is calculated from two tests, the contraction in volume on combustion of (1) the coal gas itself (with necessary dilution with pure air as already described), and (2) the air of the space.

EXAMPLE :

The coal gas itself.

Pure air for dilution	7.942 cc.
After addition of coal gas.	9.173 cc.

Therefore volume of gas used 1.231 cc.

Volume after combustion 6.856 cc.

Therefore contraction $= 9.173 - 6.856 = 2.317$ cc.

Percentage ratio of contraction to volume of gas $= \frac{2.317}{1.231} \times 100 = 188.22$.

The air in the space.

Sample taken 9.881 cc.

After combustion 9.555 cc.

Contraction 0.326 cc.

Percentage ratio of contraction to volume of air $= \frac{0.326}{9.881} \times 100 = 3.30$.

Therefore coal gas present $= \frac{3.30}{188.22} \times 100 = 1.75$ per cent.

AQUEOUS VAPOUR

The aqueous vapour in air can be estimated by aspirating a known volume, say 100 litres, through tubes packed with suitable moisture-absorbing material, such as dry pumice stone saturated with concentrated sulphuric acid. The increase in weight gives the aqueous vapour in the quantity of air used, and this is calculated to gm. per cubic metre (1000 litres). This method is rarely employed, as sufficiently accurate results can be rapidly obtained with a Mason Hygrometer (Fig. 12), or its elaborated form, the Hygrodeik (Fig. 13).

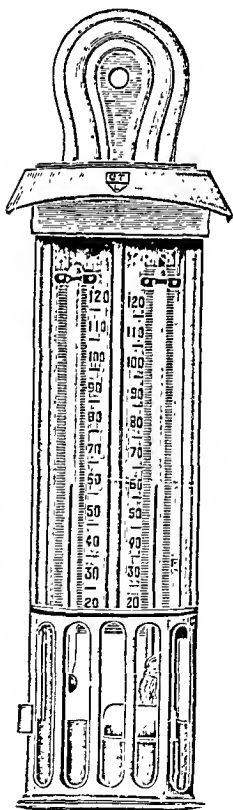


Fig. 12.

Mason's Hygrometer

The apparatus consists of two accurately graduated thermometers mounted on a suitable stand. Round the bulb of one thermometer is tied a piece of muslin, which is again connected with a wick of similar material dipping into a small vessel containing distilled water; by this means the bulb is kept constantly moist, and evaporation from its surface is continuous. The bulbs are sufficiently far apart to prevent the evaporation from the wet bulb influencing the dry bulb

thermometer. The instrument is gently swung in the air space to be examined until the mercury levels are constant ; dry and wet bulb readings are taken simultaneously. Reference is now made to tables.

TABLE FOR FINDING THE DEW-POINT¹

Dry Bulb. °F.	Factor.	Dry Bulb. °F.	Factor.	Dry Bulb. °F.	Factor.
10	8.78	41	2.26	71	1.76
11	8.78	42	2.23	72	1.75
12	8.78	43	2.20	73	1.74
13	8.77	44	2.18	74	1.73
14	8.76	45	2.16	75	1.72
15	8.75	46	2.14	76	1.71
16	8.70	47	2.12	77	1.70
17	8.62	48	2.10	78	1.69
18	8.50	49	2.08	79	1.69
19	8.34	50	2.06	80	1.68
20	8.14	51	2.04	81	1.68
21	7.88	52	2.02	82	1.67
22	7.60	53	2.00	83	1.67
23	7.28	54	1.98	84	1.66
24	6.92	55	1.96	85	1.65
25	6.53	56	1.94	86	1.65
26	6.08	57	1.92	87	1.64
27	5.61	58	1.90	88	1.64
28	5.12	59	1.89	89	1.63
29	4.63	60	1.88	90	1.63
30	4.15	61	1.87	91	1.62
31	3.70	62	1.86	92	1.62
32	3.32	63	1.85	93	1.61
33	3.01	64	1.83	94	1.60
34	2.77	65	1.82	95	1.60
35	2.60	66	1.81	96	1.59
36	2.50	67	1.80	97	1.59
37	2.42	68	1.79	98	1.58
38	2.36	69	1.78	99	1.58
39	2.32	70	1.77	100	1.57
40	2.29				

¹ *Hygrometrical Tables*, by James Glaisher, F.R.S.

TABLE OF QUANTITY¹

Showing the weight in grammes of vapour per cubic metre of air when saturated, from 0° to 100° F.

Temp. Fahr.	Weight in Gm.	Temp. Fahr.	Weight in Gm.	Temp. Fahr.	Weight in Gm.	Temp. Fahr.	Weight in Gm.
0	1.26	26	3.85	51	9.71	76	22.19
1	1.30	27	4.01	52	10.05	77	22.87
2	1.35	28	4.18	53	10.41	78	23.60
3	1.42	29	4.33	54	10.78	79	24.36
4	1.49	30	4.51	55	11.15	80	25.14
5	1.56	31	4.69	56	11.53	81	25.92
6	1.63	32	4.88	57	11.92	82	26.72
7	1.69	33	5.06	58	12.34	83	27.54
8	1.76	34	5.27	59	12.77	84	28.39
9	1.83	35	5.47	60	13.21	85	29.25
10	1.92	36	5.68	61	13.67	86	30.15
11	2.01	37	5.88	62	14.13	87	31.07
12	2.10	38	6.09	63	14.56	88	32.00
13	2.20	39	6.32	64	15.09	89	33.00
14	2.29	40	6.55	65	15.59	90	34.00
15	2.38	41	6.80	66	16.12	91	35.00
16	2.50	42	7.05	67	16.64	92	36.04
17	2.61	43	7.33	68	17.19	93	37.11
18	2.73	44	7.60	69	17.76	94	38.21
19	2.84	45	7.88	70	18.34	95	39.33
20	2.98	46	8.15	71	18.93	96	40.48
21	3.12	47	8.45	72	19.55	97	41.67
22	3.25	48	8.75	73	20.17	98	42.88
23	3.39	49	9.07	74	20.83	99	44.14
24	3.52	50	9.39	75	21.50	100	45.42
25	3.68						

¹ Calculated from Glaisher's Tables.

TABLE OF CORRECTIONS ¹

To be used when the dew-point differs from the temperature of the air in the shade.

Diff. of Temp. °F.	Correc-tion.	Diff. of Temp. °F.	Correc-tion.	Diff. of Temp. °F.	Correc-tion.	Diff. of Temp. °F.	Correc-tion.
0	0.0000	13	1.0271	26	1.0542	39	1.0813
1	1.0020	14	1.0291	27	1.0562	40	1.0834
2	1.0041	15	1.0312	28	1.0583	41	1.0854
3	1.0062	16	1.0333	29	1.0604	42	1.0875
4	1.0083	17	1.0354	30	1.0625	43	1.0896
5	1.0104	18	1.0375	31	1.0646	44	1.0917
6	1.0125	19	1.0396	32	1.0667	45	1.0937
7	1.0146	20	1.0417	33	1.0687	46	1.0958
8	1.0167	21	1.0437	34	1.0708	47	1.0979
9	1.0187	22	1.0458	35	1.0729	48	1.1000
10	1.0208	23	1.0479	36	1.0750	49	1.1021
11	1.0229	24	1.0500	37	1.0771	50	1.1042
12	1.0250	25	1.0521	38	1.0792	51	1.1062

When the dry and wet bulb readings are alike the air is saturated with moisture, and the amount present is obtained from the 'table of quantity' opposite the temperature reading. In this case the quantity is that of maximum humidity, and the absolute equals the maximum and the relative humidity is therefore 100 per cent.

EXAMPLE :

D.B.=63° F. W.B.=63° F. Aqueous vapour=14.56 gm. per cubic metre.

When the dry and wet bulbs differ the following calculation is necessary. The first step is to find the *dew-point* according to the following rule. The difference between the two thermometers is multiplied by the factor corresponding to the dry bulb (table for finding the dew-point), and the product is subtracted from the dry bulb reading; the remainder is the dew-point.

¹ *Hygrometrical Tables*, by James Glaisher, F.R.S.

EXAMPLE :

D.B.=67° F. W.B.=62° F.

Difference, $67 - 62 = 5$. Factor for 67=1.8. $1.8 \times 5 = 9.0$. $67 - 9 = 58^\circ$ F. Dew-point= 58° F.

From the dew-point the *absolute humidity* is calculated. The quantity of aqueous vapour present at the dew-point (table of quantity) is divided by the correction corresponding to the degrees of absolute dryness (table of corrections). The

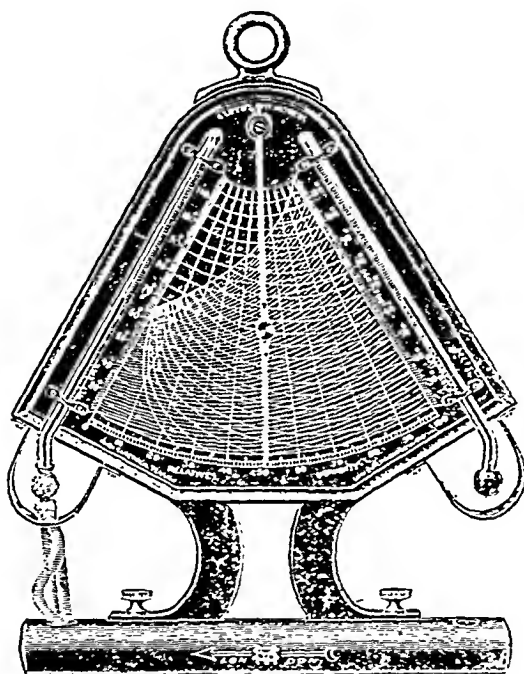


Fig. 13.

absolute dryness is the difference in degrees between the dew-point and the dry bulb reading.

Continuing the example above :

Quantity of aqueous vapour present at dew-point=12.34 gm. per cubic metre. Absolute dryness= $67 - 58 = 9$, and correction for 9=1.0187.

Then the absolute humidity = $\frac{12.34}{1.0187} = 12.11$ gm. per cubic metre.

The relative humidity, being the percentage ratio of the absolute to the maximum, = 12.11 divided by 16.64 (the maximum humidity at the dry bulb

Air

reading 67° F., see table of quantity) multiplied by $100 = \frac{12.11}{16.64} \times 100 = 72.8$.
 Relative humidity = 72.8 per cent.

Instead of swinging the hygrometer, stagnation of aqueous vapour around the wet bulb may be avoided by means of a

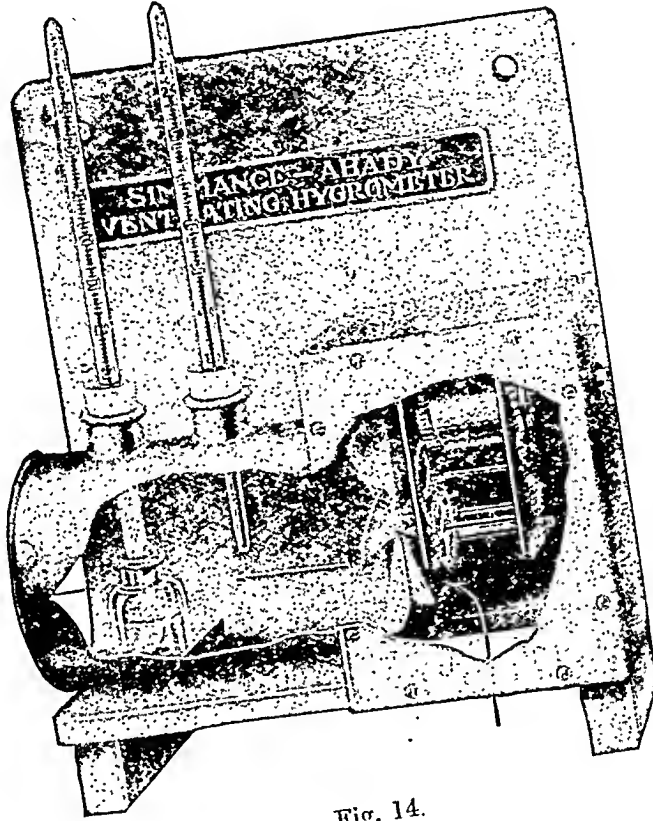


Fig. 14.

current of air. Such a ventilating hygrometer is illustrated in Fig. 14.

The Hygrodeik

Direct readings are obtained with this instrument (Fig. 13). The index hand is swung to the left of the chart, and the sliding pointer adjusted to that degree of the wet bulb thermometer at which the mercury stands. The index hand is then swung to the right, until the sliding pointer intersects the curved line which extends downwards to the left from the degree of the dry bulb thermometer scale indicated by

the top of the mercury column in the dry bulb stem. At this intersection the index hand will point to the *relative humidity* on the scale at the bottom of the chart.

EXAMPLE :

The temperature indicated by the wet bulb thermometer is 60° and that of the dry bulb 70° F. The index hand indicates relative humidity 55 per cent. when the pointer rests on the intersecting lines of 60° and 70° .

From the intersection, the curved line which passes through it, and which runs from the top downward to the right, is followed to the point of contact with the dry bulb scale. The degree at this point on that scale (53 in the example above) is the *dew-point*. The figure at the upper end of this line gives the *absolute humidity* present in grains per cubic foot of air (4.5 in this case). Grains per cubic foot can be calculated to gm. per cubic metre by multiplication with the factor 2.2894.

CARBON MONOXIDE

Qualitative Examination

(a) A strip of filter paper saturated with a 0.02 per cent. solution of palladium chloride is hung for half an hour in the space to be examined, or in a sample of 5 to 10 litres.

The appearance of a brilliant dark film of metallic palladium on the test paper indicates the presence of carbon monoxide. The test is sensitive to 1 part of carbon monoxide in 10,000 of air.

(b) Defibrinated ox blood is diluted with water until it has an apparent light yellow colour, and 10 cc. of this is shaken for half an hour with 1 litre of the sample in a bottle. Carbon monoxide renders the blood solution pink.

(c) Spectroscopic Examination.

A diluted blood solution, which has been in contact with the suspected air, is examined by the spectroscope and the appearance compared simultaneously with the untreated blood solution as a control.

To enable this to be done, the instrument should be fitted with a comparison spectrum, and it is an advantage to have a

tions are mixed directly in the absorption bulb L, Fig. 16. They are introduced through the capillary tube P. A water seal is made by placing water in bulb N, with a narrow pipette through the tube of bulb O.

PROCESS :

A sample of air is now collected and measured in the Hempel burette. This consists essentially of a graduated tube B, fixed vertically in a stand, and connected by a good length of rubber tubing from its base to the base of a tube A, also fixed vertically in a stand. The top of the graduated tube B is

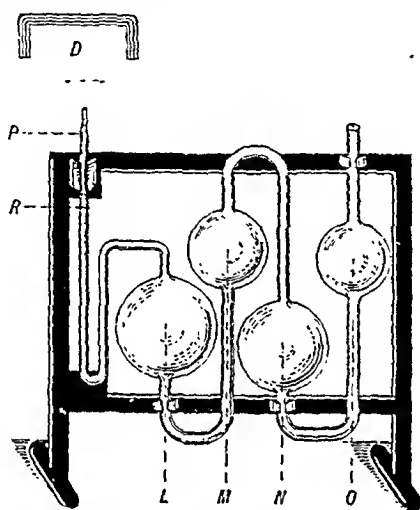
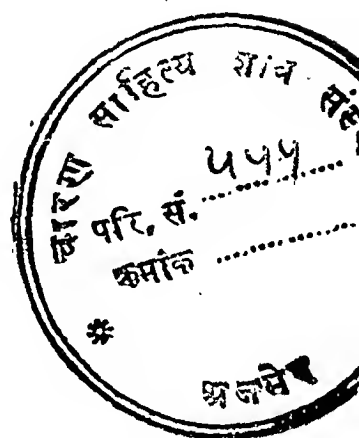


Fig. 16.

closed by a glass tap C, connected to a double-right-angled capillary tube D. The tubes A and B contain water, previously saturated with air by shaking, to the amount of about half their length, and the volume can be changed as required through the open end of tube A.

To collect a sample of air, the tube B is first completely filled with water by opening the tap C and raising the tube A until the water overflows through the capillary D. The tap C is then closed, and the sample may be taken either direct in the space or the capillary D is attached, by means of short stout rubber vacuum tubing, to the sample bottle or a tube issuing from the sample bottle, so that the two glass tubes are brought into contact. Tube A is now lowered; on opening the tap from the sample, and then slowly opening the tap C, the water gradually falls, drawing in the air; suitable means may be pro-



vided for displacing the air from the sample bottle with water. When approximately the desired amount of air has entered the burette, the tap C is closed, and the sample vessel is disconnected. The volume of the collected gas is measured after moving the tube A until the water levels in the two tubes are the same; the volume is noted.

The measured sample of air is now transferred to the absorption bulb. The fine capillary tube P is connected to a short length of vacuum tube provided with a clip; by opening this clip and aspirating through the tube, the pyrogallol solution is drawn through the capillary tube P to a mark R, and the clip is closed. The capillary D of the Hempel burette is now attached to the rubber connection of the capillary P of the absorption bulb, the glass tubes being brought as close together as possible. The tap and clip are now opened, and by raising the tube A, all the air is forced over into the absorption bulb, this being assured by allowing a little water to enter the capillary tube P. The tap and clip are closed and the absorption of the oxygen by the pyrogallol is allowed to take place for five minutes, with occasional gentle shaking, but no disconnections are made. The residual gas is then returned to the Hempel burette, by opening the tap and clip and lowering the tube A until the pyrogallol solution again reaches the mark R; the tap and clip are then closed. The volume of gas remaining is now measured, after adjusting the water levels as before and without disconnecting. It is always advisable to subject the gas to a second absorption and to continue doing so until a constant reading is obtained.

The pyrogallol solution recommended above will not give an appreciable amount of carbon monoxide. It will absorb only about twice its volume of oxygen, and consequently requires frequent changing. It should not be used at a temperature exceeding 16° C.; at room temperature three minutes with shaking ensures removal of the last traces of oxygen.

EXAMPLE :

Volume of air collected = 74.60 cc.

Volume of gas remaining = 59.25 cc.

Oxygen absorbed = $74.60 - 59.25 = 15.35$ cc.

Percentage of oxygen in the air = $\frac{15.35}{74.60} \times 100 = 20.58$ per cent.

Pyrogallol solution absorbs also carbon dioxide, consequently the reduction in volume represents oxygen plus carbon dioxide. When the latter gas is present in sufficient quantity to cause an appreciable error by this process (say 0.1 per cent.) it is estimated separately by one of the foregoing methods, and the necessary correction is made.

Phosphorus is used as an absorbent for oxygen in the form of thin sticks packed into the absorption bulb or pipette and covered with water, which is displaced by the air during the absorption. The sticks can be prepared by melting yellow phosphorus under water in a test tube, extracting portions

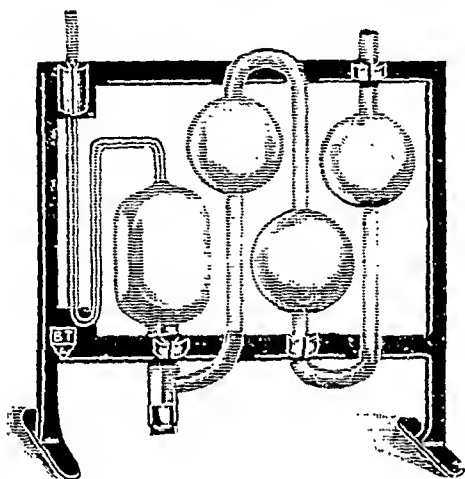


Fig. 17.

in glass tubing, and plunging the tubes into cold water; the phosphorus sets and slips out of the tube in rod form. Fig. 17 represents a very suitable form of absorption bulb for use with phosphorus. The procedure in the absorption of oxygen with phosphorus is the same as with pyrogallol. No shaking is necessary, the phosphorus, during absorption, gives a bright glow, the sudden cessation of which marks the completion of the absorption. It cannot be used in the presence of hydrocarbons, alcohol, or ammonia.

INJURIOUS GASES

Many injurious gases can be detected by smell alone, but more exact qualitative tests are carried out by means of test papers. These consist of strips of filter paper about 5×2 cm.

moistened with dilute (5 per cent.) solutions of the reagent. An example has already been given in the testing of air for carbon monoxide with palladium chloride. The strip is suspended from the hooked end of a glass rod which passes through the cork of a large sample bottle containing the air; it is allowed to remain in contact with the air for ten to fifteen minutes. The following is a summary of the tests usually applied and their indications:

Reagent.	Reaction.	Indication.
Palladium chloride.	Metallic brown stain.	Carbon monoxide.
Nessler solution.	Brown coloration.	Ammonia.
Litmus.	Red.	Acid vapours.
	Blue.	Ammonia.
	Bleached.	Chlorine, sulphur dioxide.
Lead acetate.	Brown-black stain.	Sulphuretted hydrogen.
Silver nitrate.	Brown-black stain.	Phosphoretted hydrogen.
Potassium dichromate, acidified.	Green.	Sulphur dioxide.
Starch potassium iodide.	Blue.	{ Chlorine.
		{ Oxides of nitrogen.
Starch sodium iodate.	Blue.	Sulphur dioxide.

On shaking air with pure water, a number of possible impurities are dissolved, and these can be detected in solution. The following is a scheme of tests to be applied:

Reagent.	Reaction.	Indication.
Baryta water.	White turbidity or precipitate, soluble in dilute acids.	Carbon dioxide.
Silver nitrate solution.	White precipitate, insoluble in nitric acid, soluble in ammonia.	Hydrochloric acid.
		Hydrobromic acid.
Dilute potassium permanganate solution.	Decolorised.	Sulphur dioxide.

Nitric acid, nitrous acid, and ammonia are shown by applying to this aqueous extract the characteristic tests for these impurities described under those heads in water analysis; ammonia-free water must be used.

Ammonia

The quantitative estimation of ammonia in air can be undertaken by nesslerisation of an aqueous extract of the air.

10 litres of air is aspirated through a wash bottle containing 200 cc. of ammonia-free water and 1 cc. of N/10 sulphuric acid. After aspiration, the contents of the flask are made alkaline with sodium hydroxide and examined by distillation for free and albuminoid ammonia, precisely as described in the analysis of water.

Sulphur Dioxide

A gravimetric estimation of sulphur dioxide, when abnormally large quantities are suspected, is afforded by its oxidation with bromine water (or hydrogen peroxide) contained in an absorption tower.

10 to 50 litres of air is aspirated through distilled water containing a few cc. of bromine water. The sulphuric acid formed is estimated as barium sulphate in the usual way (page 96), factor : BaSO_4 to $\text{SO}_2 = \times 0.2744$.

Arseniuretted Hydrogen

10 to 50 litres of air is aspirated through wash bottles containing lead acetate and cuprous chloride solutions, and then through a mercuric chloride test paper; the test paper is prepared by placing one drop of a 5 per cent. solution on a small piece of filter paper and drying. The formation of a yellow or orange stain indicates arseniuretted hydrogen.

Sulphuretted Hydrogen

Some indication of the quantity of sulphuretted hydrogen present in air samples is given by the intensity of the stain developed in half an hour, on a filter paper strip saturated with a 5 per cent. solution of lead acetate, when suspended in 8 litres. Pale yellow corresponds approximately to 10 parts per 10,000.

Strong yellow	„	„	50	„	„	„
Brown black	„	„	100	„	„	„

It is advisable to protect the sample test paper from light during the experiment.

Nitric and Nitrous Acids

10 litres of air is aspirated through 10 cc. of N/50 sodium

hydroxide ; this is then diluted to 100 cc. with distilled water, and well cooled, preferably to 0° C. The solution thus obtained is quantitatively examined for nitrates and nitrites as in the analysis of water.

ORGANIC MATTER

Many methods are in use for this determination, of which Carnelly's is the best, although it is not without defects ; it is based on an estimation of the oxygen (from potassium permanganate) required to oxidise the organic matter.

Solutions required :

N/100 Potassium Permanganate.

0.158 gm. pure and dry potassium permanganate is dissolved in water, and made to 500 cc. 1 cc. = 0.00008 gm. oxygen.

N/1000 Acid Potassium Permanganate.

50 cc. of the above stock solution, with 25 cc. of 10 per cent. pure sulphuric acid free from sulphur dioxide, is made to 500 cc. 1 cc. = 0.000008 gm. oxygen.

32 (molecular weight) gm. of oxygen at N.T.P. occupy 22.33 litres. \therefore 0.000008 gm. = 0.0056 cc. oxygen. \therefore 1 cc. N/1000 potassium permanganate = 0.0056 cc. oxygen.

PROCESS :

A dry glass-stoppered bottle of about 4000 cc. known capacity is filled with the sample by means of hand bellows. 50 cc. of the N/1000 potassium permanganate is introduced with a pipette, the bottle is stoppered, and the solution shaken up with the air for about 15 minutes. At the end of this time 25 cc. is poured into a 100 cc. measuring glass, and 25 cc. of the original solution is placed in a similar glass. The amount of permanganate used in the oxidation of the organic matter causes a proportionate loss of colour in the solution from the air bottle, and this is estimated by making both quantities to 100 cc. with water, and adding the original dilute standard permanganate solution, drop by drop from a burette, to the liquid from the air jar, with stirring after each addition, until the colours are matched. The number of cc. of potassium permanganate solution required to equalise the colours, multiplied

by 2 ($\frac{5.0}{2}$), gives the quantity decolorised by the volume of air, calculated to N.T.P., in the bottle, and from this the oxygen is calculated to parts per million of air.

EXAMPLE :

Volume of air taken calculated to N.T.P.=3722 cc.

Volume of air used in experiment=3722-50 cc. (volume of permanganate)=3672 cc.

25 cc. of permanganate after experiment requires 4.1 cc. of N/1000 potassium permanganate to restore its full colour.

\therefore 50 cc. requires $4.1 \times 2 = 8.2$ cc.

Now 1 cc. N/1000 $\text{KMnO}_4 = 0.0056$ cc. oxygen.

\therefore 8.2 cc. N/1000 $\text{KMnO}_4 = 0.04592$ cc. of oxygen.

\therefore 3672 cc. of sample require 0.04592 cc. of oxygen to oxidise the organic

matter = $\frac{1,000,000}{3672} \times 0.04592 = 12.51$ parts oxygen required per million.

SUSPENDED MATTER

In the open country the quantity of suspended matter in the air as dust is very minute, but in the neighbourhood of particular industrial processes the amount may be very considerable. In the latter case the nature of the dust is a factor no less important than the quantity.

The quantitative examination, which is rarely necessary, is carried out by aspirating a large quantity of the air, 100 to 500 litres, through 50 cc. of doubly-distilled water in a gas-washing bottle. The liquid is poured into a weighed platinum basin, the bottle is washed out with water, and the whole evaporated to dryness on a steam bath, and dried in a steam oven until constant in weight. The result is returned in milligrammes per cubic metre (1000 litres).

For a qualitative examination the air may be aspirated through a small open tube smeared with pure vaseline. The dust is intercepted, and can be examined microscopically by removing a small quantity of the coating and placing it on a slide; it is essential to examine the vaseline itself to ensure its purity.

W A T E R

THE object of the chemical analysis of water is to determine whether its purity is such as to warrant its use for drinking and general domestic purposes, or for some special industry. In the first case a 'sanitary analysis' would be called for, and in the second an 'industrial' analysis. The former is directed chiefly *to the detection of excretal pollution as a latent or active carrier of pathogenic organisms, and any dissolved matter which would prove injurious to health.* The industrial examination is made to determine whether its constituents would render it unsatisfactory for boiler purposes or in some particular manufacturing process. Public health analysis deals with water only from a sanitary point of view.

Sources of Supply

RAIN-WATER

Rain as it falls in the open country is very pure, but that collected in large towns is frequently unfit for potable purposes owing to pollution taken from the atmosphere. In certain remote districts rain is the only water available. It is usually collected on the roofs of buildings, and after passing through a rain-water separator is stored in tanks; the fitting of a separator is essential, for by this means the rain which has fallen first, and contains the major portion of the dirt of all kinds on the collecting surface, is deflected and does not enter the main collection. At no time can such a supply be considered really satisfactory; the washing of the collecting surface is seldom complete, and only by the exercise of great care are the storage tanks prevented from accumulating contamination. Filtration of the water before use is very necessary. One advantage of rain-water is that it contains only a small quantity of dissolved matter and is

very soft ; a disadvantage is a marked tendency to dissolve metals.

UPLAND SURFACE WATER

Mountain streams and lakes provide excellent sources of supply. The districts are sparsely inhabited, and dangerous contamination is easily guarded against. These waters contain little dissolved solids. Peat is often present in considerable quantity, and in these cases the water has a marked colour and is frequently acid in reaction.

RIVERS

Near the source rivers generally provide good water. Later the drainage from fields under cultivation, from houses, and from industries on and near their banks, causes rivers to be contaminated ; yet such supplies, after proper purification by storage and other means, are largely used in various parts of the country. The composition of river-water varies greatly according to location and to rainfall.

SPRINGS

Springs are of two kinds, 'land springs' and 'main springs.' Land springs are chiefly surface water, and main springs issue from underneath impermeable strata. The former, therefore, are frequently polluted, but main springs provide good, if not large, supplies. Land springs are generally intermittent, but main springs are usually perennial.

WELLS

Wells sunk into the permeable stratum on the surface are 'shallow wells,' and those sunk through this permeable stratum and an impermeable stratum to a lower permeable stratum are known as 'deep wells.' 'Artesian wells' are those sunk into a permeable stratum whose outcrop is at a higher level than the top of the well, so that the water rises beyond the ground surface by its own pressure ; they are frequently of great depth. Water from shallow wells is very commonly contaminated. Deep wells usually provide good and abundant supplies, but exceptions are often due to the excessive amount of dissolved solids present ; dangerous excretal contamina-

tion is rare, as the water travels a long distance through the strata.

DISTILLED WATER

On board ship sea-water and water of doubtful purity is distilled. Unless aerated it is insipid to the taste, but should be perfectly pure. Oil from the distillation machinery and traces of lead and copper are frequently present.

Collection of Water Samples

The most suitable vessels for water samples are clear-glass Winchester quart bottles ; stoneware jars should not be used, and glass stoppers are decidedly preferable to corks. Bottles which have contained ammonia are inadmissible. The bottles are cleaned by rinsing with strong hydrochloric acid and are then thoroughly washed. As a rule one Winchester quart will be found sufficient for a complete sanitary analysis.

The sample should be drawn at the same place and under exactly the same conditions as the water is, or would be, obtained for general use, and after meteorological conditions which will make it likely to contain the maximum proportion of any possible contamination. The bottle is twice rinsed out with the water and then nearly filled, the stopper is also rinsed and inserted. A piece of clean linen is tied over the stopper and sealed. It is essential that great care be exercised in taking samples of water, as the analysis is concerned with substances present in only very small amount, and faulty sampling may cause entirely erroneous results to be obtained.

The fullest possible information regarding the supply must be furnished to the examiner. The particulars to be given will include :—

1. Whether the supply is a well, lake, stream, river, spring, public supply, collected rain-water, or artificially distilled water.

- (a) Well. Depth and diameter of well, condition of repair, depth of water in well, whether water comes from underneath impermeable strata.

- (b) Stream or river. Whether flow is normal, low, or in flood.
 - (c) Public supply. Whether sample has been taken direct from the main or from a cistern.
 - (d) Collected rain-water supply. Whether a rain-water separator is fitted.
 - (e) Artificially distilled water. Water from which it is distilled.
2. Why an analysis is called for.
 3. Possible sources of pollution.
 4. Strata with which water has been in contact.
 5. Recent weather conditions regarding rainfall.

The analysis of the sample should be commenced as soon as possible, as the composition of the water may undergo appreciable alteration if this is delayed. Samples should be kept in a cool place away from light. The sample must be thoroughly shaken in each case immediately before measuring a quantity for a test.

In the first column below are given the determinations which are essential in a sanitary water analysis; further information is provided by those in the second column.

Total Solids.	Non-Volatile Solids.
Free and Saline Ammonia.	Volatile Solids.
Albuminoid Ammonia	Suspended Solids.
Nitrous Nitrogen (Nitrites)	Temporary Hardness.
Nitric Nitrogen (Nitrates).	Permanent Hardness.
Chlorine (Chlorides).	Oxygen absorbed in 2 hours at 26.5° C.
Total Hardness.	Phosphates.
Iron, Lead, Copper, Zinc.	Sulphates.
	Reaction.
	Colour.
	Clarity or Turbidity.
	Odour.
	Dissolved Oxygen.

The total solids give a general indication of the total solids in solution and in suspension. The free ammonia, albuminoid ammonia, nitrites, and nitrates determinations are the chief factors from which the absence or presence of sewage may be deduced. Chlorine provides evidence of the entry of salt

from sea-water or otherwise into a supply. The hardness determines, from one point of view, the suitability of the water for general domestic use, and the detection and estimation of metals will decide whether any danger is to be apprehended from these substances.

The results of the analysis are incorporated in the form of a report as follows :—

SAMPLE OF WATER

From :

Source :

Date : taken, ; received, ; analysed, .

Total Solids

Non-Volatile Solids

Volatile Solids

Suspended Solids

Free and Saline Ammonia

Albuminoid Ammonia

Nitrous Nitrogen (Nitrites)

Nitric Nitrogen (Nitrates)

Total Hardness

Temporary Hardness

Permanent Hardness

Chlorine (Chlorides)

Iron, Lead, Copper, Zinc

Reaction

Colour

Clarity or Turbidity

Odour

.....

.....

} parts per 100,000.

Remarks.

Signed.

Date.

Calculation of Results

In most chemical analyses it is usual to express the results in terms of percentage, but the substances in water are present in such small quantities that this would be an unsatisfactory method. Two denominations are in use, 'Grains per Gallon,'

and 'Parts per 100,000,' of which the latter is the more convenient and is used in this work.

A gallon of water weighs 10 lb., and 1 lb. contains 7000 grains, hence 1 gallon=70,000 grains, and therefore 'grains per gallon'=parts per 70,000.

To convert grains per gallon to parts per 100,000, multiply by $\frac{100,000}{70,000} = \frac{10}{7}$. To convert parts per 100,000 to grains per gallon, multiply by $\frac{70,000}{100,000} = \frac{7}{10} = 0.7$.

EXAMPLES :

13.2 grains per gallon to parts per 100,000 = $13.2 \times \frac{10}{7} = 18.86$ parts per 100,000.

6.4 parts per 100,000 to grains per gallon = $6.4 \times 0.7 = 4.48$ grains per gallon.

In water analysis a ready method of obtaining results in parts per 100,000 is to calculate to milligrammes per 100 cubic centimetres. One cubic centimetre (cc.)=1 gramme (gm.) of water, and 1 gramme=1000 milligrammes (mgm.), therefore 100 cc. of water=100,000 mgm.; and it follows that milligrammes per 100 cc.=parts per 100,000.

In the same way milligrammes per 70 cc.=parts per 70,000 or grains per gallon; the quantity 70 cc. is sometimes called a miniature gallon.

REACTION, ODOUR, COLOUR, CLARITY OR TURBIDITY

Reaction and Odour

About 150 cc. of the sample is poured into a clear-glass stoppered bottle of about 250 cc. capacity, containing a piece each of red and blue litmus paper; the stopper is inserted, the whole allowed to stand for about an hour warmed to about 50° C., and given an occasional shaking. At the end of that time the reaction can be noted by any change in colour of the test papers, and on removing the stopper any odour will be apparent.

Colour

This is determined by comparing the colour seen on looking down a 2-foot tube filled with the sample, and a similar tube filled with distilled water. It is sometimes necessary to determine the colour quantitatively, and this can be done with any of the various instruments designed for the purpose. In the Burgess colorimeter (Fig. 18), by means of a standard solution of 1 gm. of crystallised cobalt sulphate and 0.05 gm. potassium dichromate per litre, distilled water in a 2-foot tube A is made to match the colour of the sample contained in a similar tube B, and the depth in millimetres of the quantity of standard solution required in F is recorded.

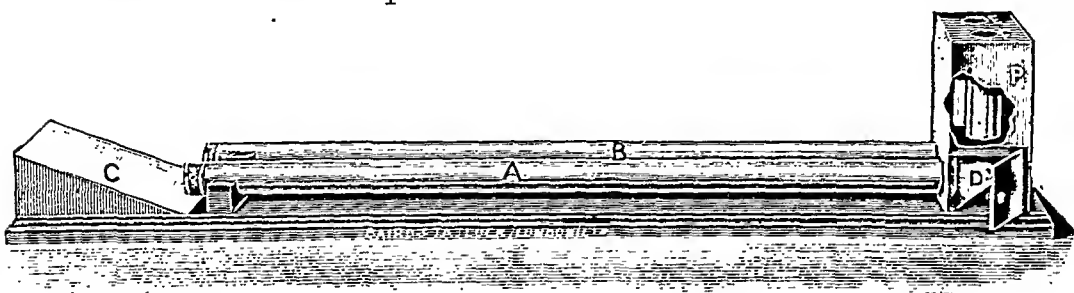


Fig. 18.

Clarity or Turbidity

A small quantity of the sample is poured into a test glass and its appearance noted. As in the case of colour, quantitative determinations can be made with special apparatus; one method is to note the depth at which a piece of platinum wire of standard dimensions disappears from view.

Aeration

The degree of aeration is seen by the liberation of gas bubbles on shaking.

TOTAL SOLIDS : NON-VOLATILE SOLIDS ; VOLATILE SOLIDS ; SOLIDS IN SUSPENSION ; SOLIDS IN SOLUTION
PROCESS :

Total Solids

A platinum basin is weighed, and after thoroughly shaking the sample, 50 cc. is placed in the dish. The water is evaporated to dryness on a steam bath, the outside of the basin is

carefully wiped with a clean cloth damped with distilled water, the basin is transferred to a hot-air oven at a temperature of 105 to 108° C., and heated for one hour. It is then removed to a desiccator and, when cold, weighed, afterwards reheated for a further period of half an hour and weighed again. The weight should be the same or only slightly less than the first; if more than 1 mgm. loss has occurred, further heating and weighing is necessary. The final weight, less the weight of the basin, is the weight of total solids in 50 cc. The weighing must be carried out very quickly, as water solids rapidly absorb moisture from the air; the first weight of the basin and residue should be on the balance before the second weighing is commenced.

Non-Volatile Solids

The basin containing the total solids is heated over an argand burner for half an hour, weighed after cooling in a desiccator, and reheated and reweighed as before. The weight of solid matter now remaining represents the non-volatile solids.

Volatile Solids

By difference: total solids—non-volatile solids=volatile solids.

EXAMPLE: 50 cc. of sample taken.

Total Solids.

Weight of basin+solids	34.2815 gm. (1st)
	34.2810 „ (2nd)
Weight of basin	34.2635 „
Weight of solids	<u>0.0175 „</u>

Non-Volatile Solids.

Weight of basin+solids	34.2785 gm. (1st)
	34.2785 „ (2nd)
Weight of basin	34.2635 „
Weight of solids	<u>0.0150 „</u>

Total solids=17.50 mgm. in 50 cc.=35.00 mgm. in 100 cc.=35 parts per 100,000.

Non-volatile solids=15.00 mgm. in 50 cc.=30.00 mgm. in 100 cc.=30 parts per 100,000.

Volatile solids=total solids—non-volatile solids=35.00—30.00=5 parts per 100,000.

Attention is drawn to this method of recording the weights.

Suspended Solids

It is usually only necessary to record the suspended solids as 'Small quantity,' 'Trace,' 'Nil,' etc., as the case may be, but when present in amount sufficient to render the water turbid a quantitative determination may be required. A filter paper of convenient size is placed in a weighing bottle, and the whole dried in the water oven until constant in weight. The stopper is, of course, removed during the process of drying, and is kept apart until immediately before placing the bottle on the balance; if previously inserted the bottle may crack on cooling in the desiccator. The filter paper is placed in a funnel, and 500 cc. of the sample is filtered, and the residue washed with distilled water. The filter paper containing the suspended solids is now replaced in the weighing bottle, and the whole dried as before until constant in weight. The increase in weight represents the suspended solids.

EXAMPLE : 500 cc. taken.

Wt. of weighing bottle + filter paper + suspended solids	20.2810 gm. (final)
Wt. of weighing bottle + filter paper	20.2625 „ (final)
Wt. of suspended solids	<u>0.0185 „</u>
= 18.5 mgm. in 500 cc. = 3.70 mgm. in 100 cc.	
= 3.70 parts per 100,000.	

Solids in Solution

If this is required it can be calculated by difference; total solids—suspended solids=solids in solution.

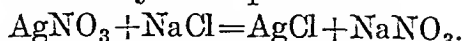
E.g. from the above figures, 35.00—3.70=31.30 parts per 100,000.

CHLORINE AS CHLORIDES

Solutions required

Standard Silver Nitrate. 4.7910 gm. pure recrystallised silver nitrate per litre, 1 cc.=1 mgm. chlorine.

The chemical reaction between silver nitrate and a soluble chloride is represented by the equation :



Calculating from atomic weights, 169.89 gm. of silver nitrate precipitates 35.46 gm. of chlorine as silver chloride; to pre-

precipitate 1 gm. of chlorine 4.7910 gm. of silver nitrate is required, and if this quantity is dissolved in water and made to 1000 cc., 1 cc. of the solution will precipitate $\frac{1}{1000}$ part of a gm. = 1 mgm. chlorine.

Potassium Chromate, as indicator.

10 per cent. solution free from chlorine.

With silver nitrate and potassium chromate a red precipitate of silver chromate is formed; however, if a soluble chloride and potassium chromate are together in solution, the red silver chromate does not form until all the chlorine has been first precipitated. Immediately, therefore, a permanent red precipitate is obtained, it is known that sufficient silver nitrate has been added to precipitate all the chlorine.

Process:

100 cc. of the sample is measured into a porcelain basin and just sufficient potassium chromate is added to give the water a faint yellow colour. Standard silver nitrate, from a burette, is run in, with stirring after each addition, until the formation of silver chromate is indicated by the presence of a faint trace of permanent red colour. Each cc. of the standard solution used denotes 1 mgm. of chlorine present in 100 cc. of the sample = 1 part per 100,000.

EXAMPLE.

100 cc. of the sample required 2.7 cc. standard silver nitrate = 2.7 parts of chlorine per 100,000.

If the water is markedly acid it must be neutralised with calcium carbonate (free from chlorides) before titration and filtered, as the silver chromate is soluble in acid solution. Sulphuretted hydrogen, if present, is removed by boiling the quantity taken; after cooling, this is made up to approximately the original volume with distilled water. It is necessary that the water be cold before titration.

It is sometimes desirable to return the chlorine in terms of sodium chloride (ordinary salt), in which form it is most commonly present in water.

Sodium chloride, NaCl (filling in atomic weights) = 23.00 + 35.46 = 58.46—that is, 35.46 gm. of chlorine is equal to 58.46 gm. of NaCl.

1 gm. of chlorine therefore = $\frac{58.46}{35.46} = 1.649$ gm. of sodium chloride.

To express chlorine in terms of sodium chloride, it is therefore necessary to multiply by 1.649.

Free Chlorine

Hypochlorites are extensively used for the sterilisation of water on account of the great efficiency of free chlorine and the minute proportion required. It may be occasionally necessary to examine for chlorine in this form.

A simple and rapid test is to add to 100 cc. of the sample, 2 cc. of freshly prepared starch solution (page 80) containing 5 per cent. of potassium iodide. Free chlorine liberates iodine from the potassium iodide, and this gives an immediate blue colour with the starch solution. A colour produced only after the elapse of a few seconds can be ignored.

FREE AND SALINE AMMONIA, AND ALBUMINOID AMMONIA

Solutions required:

Sodium Hydroxide

30 gm. is dissolved in 350 cc. of water and the solution boiled to 250 cc. to remove any traces of ammonia.

Nessler Solution

13 gm. of mercuric chloride is dissolved in 200 cc. of water and 35 gm. of potassium iodide in another 200 cc. of water; each solution is boiled. The two solutions are mixed hot, and then a saturated solution of mercuric chloride is added until a permanent red precipitate is obtained. The mixed solution is boiled, cooled, and when quite cold, is decanted from the precipitate produced. 120 gm. of potassium hydroxide, previously dissolved in about 500 cc. of water and cooled, is added, and the whole made to 1 litre. The Nessler solution is stored in a well-corked bottle and decanted from any precipitate into a suitable bottle when required. Should the solution lose

its sensitiveness, as shown by the loss of its proper yellow colour, this can be restored by the addition of a few drops of saturated mercuric chloride solution.

Standard Ammonium Chloride, 1 cc. = 0.01 mgm. NH_3 .

From atomic weights, 53.50 NH_4Cl contains 17.03 NH_3 ; and therefore 3.1415 gm. of ammonium chloride contains 1 gm. of ammonia. If this quantity is dissolved in water and made to 1 litre, 1 cc. of the solution will contain $\frac{1}{1000}$ of a gm. = 1 mgm. of ammonia. This solution is diluted 1 in 100 with ammonia-free distilled water, then 1 cc. = 0.01 mgm. NH_3 .

Ammonia-free Distilled Water

Ordinary tap water, made distinctly acid with sulphuric acid, is distilled. The distillate is discarded until, on testing with Nessler solution, complete absence of ammonia is indicated; it is then collected and stored in well-stoppered bottles.

Alkaline Permanganate

200 gm. of potassium hydroxide and 8 gm. of potassium permanganate are dissolved in about 1500 cc. of water; the solution is boiled until reduced to less than two-thirds in volume, and when cold made to 1 litre with ammonia-free distilled water.

Process:

The ammonia is separated by distilling the water after the addition of necessary reagents, and is estimated in the distillate.

The distilling apparatus, consisting of a flask of about 1500 cc. capacity, with a bent tube connection to an efficient condenser, is fitted up after each of the parts has been thoroughly washed. For all washing purposes in the process ordinary tap water is used. The corks should be covered with tin-foil; rubber stoppers must not be employed. The quantity of ammonia may be extremely minute, and every trace of ammonia must first be removed from the apparatus before the analysis proper can be undertaken. This is effected by means of a preliminary distillation. The flask is removed, and to it is added 2 cc. of the sodium hydroxide solution, about 1200 cc. of ordinary distilled water, and, to prevent bumping, a few small pieces of broken porcelain. The apparatus is recon-

nected and distillation commenced. The first 200 cc. of distillate is neglected; it is then collected in 50 cc. fractions in nessler glasses which have been carefully washed out. The nessler glasses are colourless, and should hold about 130 cc.; they have only two graduations, a 50 cc. and a 100 cc. mark, which are at the same height from the bottom in each. To each fraction 2 cc. of the nessler solution is added; this process is called 'nesslerising.' A short-nosed pipette should be used; if allowed to stand in the bottle, it is only necessary to withdraw the pipette and let the solution run down to the mark; sucking up by mouth, with its attendant risk of injury, is thus avoided. Any ammonia contained in the distillate will produce, with the nessler solution, a yellow colour (if in large quantity a precipitate) which varies in intensity directly according to the quantity of ammonia present. The colour is observed when the glasses are standing on a white surface, and as the apparent colour is materially altered if liquid intervenes between the glass and the surface, any external liquid must be removed. The distillation is continued until a fraction gives no reaction with the nessler solution, showing that the apparatus and the contents of the flask are free from ammonia. If ammonia-free distilled water is used in the flask to effect this, the apparatus will more quickly become ammonia-free, but the advantage is scarcely commensurate with the trouble necessary to prepare the special distilled water; ordinary distilled water necessitates a longer distillation, as it generally contains a small quantity of free ammonia.

Free and Saline Ammonia

To the liquid remaining in the flask after the preliminary distillation, there is added a definite volume of the sample (measured in a graduated flask which has been very thoroughly washed out), the apparatus is reconnected, and distillation again commenced. The usual quantity of the water taken is 500 cc., but one must be guided by circumstances. It is well to make a preliminary test by nesslerising 50 cc. of the sample direct; if much colour is observed (indicating a high free-ammonia content), a smaller amount is used according as experience will show to be most suitable.

Free ammonia is ammonia existing actually free in the water; saline ammonia is that present as salts. By the action of the sodium hydroxide, which was added at the beginning of the process, the saline ammonia is liberated, and on distillation is evolved in the free state together with the free ammonia originally present. The total ammonia which distils is estimated, and the result is known under the one name of 'free ammonia.' The albuminoid ammonia is estimated after all the free and saline ammonia has been removed; this ammonia is produced by the action of a strong solution of alkaline permanganate on nitrogenous organic matter present. The two determinations, though entirely distinct, are thus carried out on the same portion of water, and the albuminoid ammonia estimation immediately follows that of the free ammonia.

The free ammonia is collected in 50 cc. fractions as it distils, and the quantity of ammonia present in each fraction is estimated separately. Each fraction is nesslerised, and as the colour produced is proportionate to the amount of ammonia present, the ammonia is estimated by making a standard, with the standard ammonium chloride solution, which will match the colour of the fraction and contain a known quantity of ammonia. The colour does not reach its maximum immediately, but does so after standing for about four minutes; this is assisted by shaking the nessler glass very gently in a longitudinal rotary movement. It is essential that nothing be allowed to come in contact with the liquid, and the nessler glasses must be thoroughly washed out each time before using. After standing for about four minutes, the colour, if any, of the first fraction is observed, and a standard made to match it. The judging of the correct standard is, of course, a matter of experience, but does not present much difficulty after a little practice. Supposing the colour indicates a 2 cc. standard, then 2 cc. of the standard ammonium chloride solution is run into a nessler glass, from a burette, made to 50 cc. with ammonia-free water, nesslerised, and the whole gently shaken and allowed to stand. When the maximum colour has developed it is compared, in a good light, with that of the fraction and, if the colours match, the standard is noted; if it does not

match, a fresh standard, containing more or less ammonium chloride as may be necessary, is prepared. It is important to notice the order in which the liquids are added in the preparation of the standard; the nessler solution is always added last, otherwise a cloudiness will result which prevents correct matching. Each fraction is estimated in the same manner, and the distillation is continued until a fraction is obtained which contains no ammonia, as shown by nesslerisation. The ammonia-free water should always be tested before use to make sure of its freedom from ammonia. The standard required in each case is noted, and the method of calculating the result will be seen in the following example:—

500 cc. of the sample required for 1st fraction	.	.	1.8 cc. standard
2nd „	.	.	1.0 „
3rd „	.	.	0.7 „
4th „	.	.	0.3 „
5th „	.	.	0.1 „
(6th free)	Total		<u>3.9 cc. „</u>

That is to say, the free (free and saline) ammonia in 500 cc. of the sample is equal to the amount of ammonia contained in 3.9 cc. of the standard ammonium chloride solution.

Now 1 cc. of the standard solution = 0.01 mgm. NH_3 ,

∴ 3.9 cc, „ „ „ = 0.039 „

∴ there is 0.039 mgm. NH_3 in 500 cc. of the sample,

= 0.0078 mgm. NH_3 in 100 cc.,

= 0.0078 parts free (free and saline) ammonia per 100,000.

An easy method of calculation is to remember that each cc. of standard solution, required for 500 cc. of the sample, is equal to 0.002 parts per 100,000. Wanklyn, the originator of the process, states, 'The first 50 cc. invariably contains three-quarters of the total amount of free ammonia,' and continues that it is only necessary to add one-third to the quantity found in it to obtain the total amount present in the volume of sample taken for the test.¹ The statement is altogether too sweeping, and our experience is that, far from being invariably the case, it is rarely so.

Albuminoid Ammonia

50 cc. of the alkaline permanganate solution is measured

¹ Wanklyn, *Water Analysis*, eleventh edition, 1907.

into a beaker, 50 cc. of ammonia-free distilled water added, and the whole is boiled down to 50 cc. to remove any trace of ammonia. The alkaline permanganate solution should be boiling ready for use, before the free ammonia estimation is finished, so that there is no delay between the determinations. The free-ammonia determination having been completed, the boiling solution is added to the boiling liquid remaining in the flask and distillation continued. If the boiling is interrupted 'bumping' is apt to ensue; no loss of ammonia occurs when the apparatus is reconnected quickly. The albuminoid ammonia, in the quantity of the sample originally taken for the test, is now evolved as ammonia, and is estimated in precisely the same manner as was the free ammonia; the calculation is also the same. It is important that the volume of liquid in the flask should not be allowed to fall below about 200 cc.; should it do so, ammonia-free distilled water must be added. If the process has been carried out as detailed here, addition to the liquid will rarely be necessary.

EXAMPLE :

500 cc. of the sample required for 1st fraction	.	.	2.0 cc. standard
2nd "	.	.	2.2 "
3rd "	.	.	1.7 "
4th "	.	.	0.9 "
5th "	.	.	0.5 "
6th "	.	.	0.3 "
7th "	.	.	0.1 "
(8th free)	Total		<u>7.7 cc.</u> "

That is to say, the albuminoid ammonia in 500 cc. of the sample is equal to the amount of ammonia contained in 7.7 cc. of the standard ammonium chloride solution.

Now 1 cc. of the standard solution = 0.01 mgm. NH_3 ,

\therefore 7.7 cc. " " " = 0.077 "

\therefore there is 0.077 mgm. NH_3 in 500 cc. of the sample,

= 0.0154 mgm. NH_3 in 100 cc.,

= 0.0154 parts albuminoid ammonia per 100,000.

NITRITES

It is usually only necessary to make a qualitative test for nitrites, but when required this is made quantitative. Nitrites oxidise rapidly to nitrates, and unless the determination

is carried out immediately after the sample has been taken, the quantity may be perhaps only a small proportion of the original amount in the water. After the lapse of a short time oxidation of the nitrites may indeed be complete, and the tests will give no indication of their former presence.

We believe, however, that the reaction is not so rapid as is commonly supposed ; we have found sealed samples, originally polluted only in slight degree, to give a very distinct indication of nitrites after standing three weeks, or more, at ordinary temperature.

The most satisfactory method for detecting and determining nitrites in water is that of Lombard.¹ It is extremely sensitive.

Lombard's Method

Solutions required :

Lombard's Reagent.—1 gm. of sulphanilic acid is dissolved, by the aid of heat, in 100 cc. of saturated ammonium chloride solution. To this is added 1.5 gm. of phenol, and finally 100 cc. of approximately 2N hydrochloric acid.

Liquor Ammonia, sp. gr. 0.880.

Standard Potassium Nitrite, 1 cc.=0.01 mgm. nitrogen as nitrites.

From atomic weights, 85.11 gm. of KNO_2 contains 14.01 gm. N. \therefore 6.0749 gm. of potassium nitrite contains 1 gm. of N. If this quantity is dissolved in water and made to 1 litre, 1 cc. of the solution will contain 1 mgm. N as nitrites.

The above solution is diluted 1 in 100, then 1 cc.=0.01 mgm. N. This solution is unstable and must be freshly prepared each time it is required.

Process:

50 cc. of the sample is placed in a 100 cc. cylindrical measuring glass ; to it is added 1 cc. of the reagent, and mixed by stirring with a glass rod. The whole is allowed to stand for fifteen minutes ; 1 cc. of ammonia is then added and mixed. If nitrites are present an orange-yellow colour will be produced which varies in intensity directly according to the quantity of nitrites present ; a control test should always be made by

¹ Maurice Lombard, *Bull. Soc. Chem.*, Paris, 1913, p. 304.

comparing the colour with a similar quantity of the sample in another glass, and to which ammonia only has been added.

If a quantitative determination is required, 5 cc. of the standard potassium nitrite solution is placed in another similar 100 cc. measure, diluted with distilled water to the 50 cc. mark, and the reagents are added as above ; a marked colour is produced. The liquids in each glass are made to 100 cc. with distilled water, and each separately mixed by placing the palm of the hand tightly on the open end of the glass and inverting two or three times. As the nitrites present in each glass produce a proportionate amount of colour, it is possible to determine the quantity of nitrite present in the sample from the dilution necessary to equalise the depth of colour in each. In the probable event of the colours not matching in the first instance, trial dilutions are made in the following manner. Into another glass, similar to those already used; there is added, say, 10 cc. of the liquid which has the deeper colour ; this is made to 100 cc. with distilled water and mixed. By looking down through the glasses the colour of this diluted liquid is compared with that which was less intense. If they are unequal further trials are made until a match is obtained.

The method of calculating the result will be seen in the two following examples :—

(a) When the colour given by the standard solution is deeper than that given by the sample.

(b) When the above positions are reversed.

(a) 50 cc. of the sample and 5 cc. of the standard potassium nitrite solution were used, and after obtaining the colours both were made to 100 cc. The glass containing the *standard* solution was the more intense in colour, and it was found that 7 cc. (of the 100 cc.) of the liquid, diluted with distilled water, matched the colour in the glass containing the sample. That is to say, 50 cc. of the sample contains an amount of nitrite equal to the quantity present in $\frac{7}{100}$ of 5 cc. of the standard potassium nitrite solution.

Now 1 cc. of the standard solution = 0.01 mgm. N as nitrites,

∴ 5 cc. „ „ „ = 0.05 mgm. N „

∴ $\frac{7}{100}$ (0.07) of 5 cc. of the standard solution = 0.0035 mgm. N,

∴ 50 cc. of the sample contains 0.0035 mgm. N,

∴ 100 cc. „ „ „ 0.007 mgm. N,

∴ N as nitrites = 0.007 parts per 100,000.

(b) 50 cc. of the sample and 5 cc. of the standard potassium nitrite solution were used, and after obtaining the colours both were made to 100 cc. The glass containing the *sample* was the more intense in colour, and it was found that 90 cc. (of the 100 cc.) of the liquid, diluted to 100 cc. with distilled water, matched the colour in the glass containing the standard solution.

That is to say $\frac{90}{100}$ of 50 cc. of the sample = 45 cc., contains an amount of nitrite equal to the quantity of nitrite present in 5 cc. of the standard potassium nitrite solution.

Now 1 cc. of the standard solution = 0.01 mgm. N as nitrites,

∴ 5 cc. " " " = 0.05 mgm. N,

∴ 45 cc. of the sample contains 0.05 mgm. N,

∴ 100 cc. " " " 0.111 mgm. N,

∴ N as nitrites = 0.111 parts per 100,000.

Another method of detecting and estimating nitrites, but one which is not so satisfactory as the foregoing, is the starch iodide method.

Starch Iodide Method

Reagents required:

Sulphuric Acid, 30 per cent.

Starch Solution.—1 gm. rice starch is made into a paste with distilled water; this is added to 200 cc. of boiling distilled water, and the boiling continued for about three minutes. The solution is made quite cold, allowed to settle, and then decanted. It should be prepared fresh each time it is required.

Potassium Iodide, solid.

Standard Potassium Nitrite Solution. 1 cc. = 0.01 mgm. N as nitrites.

Process:

In a 100 cc. cylindrical measuring glass there is placed 100 cc. of the sample, and in another similar glass 100 cc. of distilled water. To each there is added 2 cc. of sulphuric acid, a small crystal of potassium iodide, and finally 2 cc. of starch solution; the liquid in each is mixed by stirring with a glass rod. If nitrites are present in the sample, a blue colour is produced immediately, or almost immediately; the distilled water acts as a control and should remain colourless. The coloration is due to the liberation of iodine, which produces

a blue colour with starch solution ; the intensity of the colour is proportionate to the amount of nitrite present.

The reagents must be absolutely pure, and the use of a control to confirm this is essential ; iodine and starch give no colour in hot solution. To make a quantitative determination, the standard potassium nitrite solution is run into the control glass, from a burette, until the colour produced is equal to that present in the glass containing the sample ; the liquid is stirred with a glass rod after each addition.

EXAMPLE :

100 cc. of the sample was taken, and the colour was matched by the addition of 0.35 cc. of the standard solution to the control glass. That is to say, 100 cc. of the sample contains an amount of nitrite equal to the quantity present in 0.35 cc. of the standard potassium nitrite solution.

Now 1 cc. of the standard solution = 0.01 mgm. N as nitrites,
 \therefore 0.35 cc. „ „ „ = 0.0035 mgm. N,
 \therefore 100 cc. of the sample contains 0.0035 mgm. N,
 \therefore N as nitrites = 0.0035 parts per 100,000.

If the colour in the sample glass is too deep to permit accurate matching, it is diluted, and the dilution is allowed for in the calculation. The determination must be carried out rapidly because the colour deepens in contact with air.

NITRATES

Phenolsulphonic-Sulphuric Acid Method; Frederick's Modification ¹

Solutions required:

Standard Potassium Nitrate Solution.—1.4434 gm. of pure KNO_3 per litre, 25 cc. = 5.0 mgm. N as nitrates ; this solution is diluted 1 in 50, then 25 cc. = 0.1 mgm. N as nitrates.

Phenolsulphonic-Sulphuric Acid Mixture.—4 gm. of phenol (Calvert's No. 1 is very suitable) is mixed with 4 cc. of ammonia-free distilled water, and 100 cc. of concentrated nitrogen-free sulphuric acid is added ; the whole is heated at 80 to 85° C. for six hours, cooled, and made to 500 cc. with ammonia-free water. 300 cc. of concentrated nitrogen-free sulphuric acid,

¹ *Analyst*, August 1919, pp. 281-284.

made to 500 cc. with ammonia-free distilled water, is added and mixed with the foregoing solution to give one litre of reagent.

Process:

Spherical bottomed, $3\frac{1}{2}$ -inch diameter porcelain basins are used, each containing a small glass rod. To one basin 25 cc. of the sample is added, and to the other 25 cc. of the dilute standard potassium nitrate solution. 2 cc. of the phenol-sulphonic-sulphuric acid mixture is added to each and thoroughly mixed by stirring. Both are evaporated on the steam bath until no more water is expelled, and the residual liquid assumes a dark colour ('acid dryness'). During the progress of the evaporation the liquid is occasionally stirred, and any dark spots, on the side of the basin above the surface of the liquid, are incorporated in the bulk of the residue by touching with the glass rod. The basins are then removed from the steam bath, and by gently tilting them and directing the liquid with the rod, the residue is made to come into contact with all parts of the inside of the basin. All material on the sides of the basin is washed to the bottom with a very fine jet of ammonia-free distilled water; the 5 to 10 cc. required is mixed with the bulk by stirring, and the whole is again evaporated to 'acid dryness.' The residue is once more taken up with water and evaporated to 'acid dryness,' as already described. The final residues are taken up with water and poured into thin, colourless, 100 cc. measuring glasses, and the basins are washed out with small quantities of water to about 95 cc.; 3 cc. of strong ammonia (sp. gr. 0.880) is added, and the whole is made to 100 cc. The contents of each glass are separately mixed by placing the palm of the hand tightly on the open end of the glass and inverting four or five times; to prevent loss of liquid, one edge of the lip of the glass is pressed tightly against the palm in withdrawing. The colour obtained in each glass is proportionate in intensity to the quantity of nitrate originally present.

The liquid derived from the standard solution has a marked yellow colour, and that from the sample, if nitrates are present, will also be coloured. As the colours vary in intensity directly according to the quantity of nitrates present, the amount in

the sample is determined by the dilution necessary to equalise the depth of colour in each glass. The dilutions are made in exactly the same manner as described in the Lombard process for nitrates (page 78), and the calculation of the result is also similar.

A solution of potassium hydroxide may be used in place of ammonia, but is only satisfactory when prepared the same day. The colour obtained with a sample must always be compared with a standard prepared by the same process. In the few cases where the quantity of nitrogen as nitrates in a sample approximates or exceeds 4.0 parts per 100,000, the determination is repeated, using only 10 cc. of the sample; in 500 consecutive samples analysed by one of us, received from every kind of supply in all parts of the United Kingdom, this quantity was only exceeded three times.

This modification eliminates the considerable error which is caused in the original process by the presence of chlorides.

EXAMPLES :

(a) 25 cc. of the sample and 25 cc. of standard potassium nitrate solution were evaporated, and after obtaining the colours both were made to 100 cc. It was found that 18 cc. of the liquid derived from the *standard* solution, made to 100 cc., matched the colour in the glass containing the sample. That is to say, 25 cc. of the sample contains an amount of nitrate equal to the quantity present in $\frac{18}{100}$ of 25 cc. of the standard potassium nitrate solution.

Now 25 cc. of the standard solution = 0.1 mgm. N as nitrates,

∴ 25 cc. of the sample contains $\frac{18}{100}$ (0.18) of 0.1 mgm. = 0.018 mgm.

∴ 100 cc. „ „ „ 0.072 mgm. N.

N as nitrates = 0.072 parts per 100,000.

(b) The same quantities of sample and standard were used as in the above example, and it was found that 65 cc. of the liquid derived from the *sample*, made to 100 cc., matched the colour in the glass containing the standard. That is to say, $\frac{65}{100}$ of 25 cc. of the sample contains an amount of nitrate equal to the quantity present in 25 cc. of the standard potassium nitrate solution.

Now 25 cc. of the standard solution = 0.1 mgm. N as nitrates,

∴ $\frac{65}{100}$ (0.65) of 25 cc. = 16.25 cc. of the sample, contains 0.1 mgm. N,

∴ 100 cc. of the sample contains 0.515 mgm. N.

N as nitrates = 0.515 parts per 100,000.

If a very large quantity of organic matter is present in the water, charring occurs with the phenolsulphonic-sulphuric acid, and any colour present after adding ammonia or potassium hydroxide is more or less masked. In such cases it is advisable previously to clarify the sample.

Preliminary Clarification:

Alumina Cream

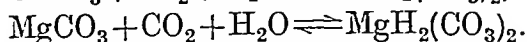
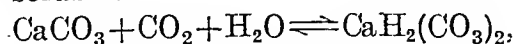
Pure aluminium sulphate is dissolved in boiling water, and excess of liquor ammonia (sp. gr. 0.880) is then added.

The whole is boiled until no smell of ammonia is perceptible and, after the boiling has been allowed to continue for a few minutes longer, is filtered. The aluminium hydroxide is washed very thoroughly with boiling water, and is then mixed with a small quantity of water; the cream is stored in a tightly stoppered bottle.

To 50 cc. of the sample is added about 10 cc. of alumina cream, and the whole is allowed to stand, with occasional shaking, for an hour. On filtering it will be found that any turbidity and colour has been removed. The residue on the filter paper is washed until the total filtrate, collected in a graduated flask, measures exactly 100 cc.; the filtrate is mixed and 50 cc. is taken, equal to 25 cc. of the original sample. After this preliminary preparation of the water the process proceeds as already described.

HARDNESS

The hardness of water is due almost entirely to the presence in solution of the bicarbonates, sulphates, and chlorides of calcium and magnesium; the calcium salts predominate. The carbonates are almost insoluble in water, but in the presence of dissolved carbon dioxide they form bicarbonates which are soluble.



The bicarbonates are unstable, and on boiling they are decomposed in a manner the reverse of the way in which they are produced, and the calcium and magnesium, present as bicarbonates, is almost completely precipitated as

carbonate. As the hardness due to these bicarbonates is thus practically destroyed by boiling, it has received the name of 'temporary' hardness. The hardness due to the sulphates and chlorides is unaffected by boiling, and is known as 'permanent' hardness.

It is usual to estimate the total and the permanent hardness, and then, by difference, to obtain the temporary hardness. In a sanitary water analysis it is not necessary to determine the quantities of calcium and magnesium salts themselves, but simply the soap-destroying power of the water. Soaps are sodium or potassium salts of certain fatty acids, and, when in contact with the calcium and magnesium salts causing the hardness of the water, double decomposition takes place, with the formation of insoluble calcium and magnesium salts of the fatty acids. Thus an amount of soap is destroyed proportionate to the quantity of calcium and magnesium salts originally in solution. A persistent lather with soap and water is not obtained until all the hardness has been precipitated in this manner and an excess of soap is present.

Solutions required:

Standard Hard Water. 1 cc.=1 mgm. calcium carbonate.

1 gm. of selected Iceland spar (crystalline calcium carbonate) is weighed in a small porcelain basin and about 10 cc. of distilled water added. While the basin is covered with a clock glass, concentrated hydrochloric acid is added, a few drops at a time, until effervescence ceases, showing that solution of the calcium carbonate as calcium chloride is complete. The glass is gently raised, and any liquid which has spirted on to the bottom, washed into the basin; the whole is evaporated to dryness on a steam bath. The residue is taken up with a little distilled water, and the solution again evaporated to dryness; this process is repeated four times, and then the whole is heated on a hot plate for two hours, to ensure that all traces of acid are removed. The residue from the final evaporation is dissolved in distilled water and made to 1 litre; the distilled water is previously boiled to remove dissolved carbon dioxide, and cooled.

1 cc. of the solution has a soap-destroying power=1 mgm. calcium carbonate.

Standard Soap Solution. 1 cc.=1 mgm. hardness as calcium carbonate.

Half a cake of Pears' soap is cut into fine shreds and shaken with a mixture of approximately equal parts of alcohol and distilled water; the whole is allowed to stand and filtered. The solution is standardised in the following manner: 20 cc. of standard hard water is measured into a 300 cc. stoppered bottle and 80 cc. of cold, freshly boiled, distilled water is added. The soap solution is run in from a burette, at first 1 cc. and then, when the reaction is nearly complete, 0.5 cc. at a time, thoroughly shaking after each addition. The end of the reaction is indicated by the formation of a lather which persists for two minutes.

The occasional phenomenon of 'false' lather must be guarded against, *i.e.* the production of an apparent lather when the reaction is incomplete. For this reason, when the reading has been taken, a further 2 cc. of soap solution is added and shaken. If the original amount added was the true one, an excessive lather will be obtained; if there was a false lather it will have more or less completely disappeared, and the addition of soap solution, 0.5 cc. at a time, is continued until a true lather is obtained; only the quantity required to produce the true lather is noted.

The last quantity of soap solution added, *i.e.* 0.5 cc., is the excess necessary to produce the lather, and is deducted from the total quantity required in each titration in order to obtain the amount necessary to precipitate the hardness only.

As 1 cc. of the standard hard water equals 1 mgm. CaCO_3 , then 20 cc. of standard hard water equals 20 mgm. CaCO_3 . Therefore, if the soap solution were exactly correct, 20 cc. would be required to precipitate the hardness in 20 cc. of standard hard water, and to obtain a lather a further addition of 0.5 cc. would be required, *i.e.* a total of 20.5 cc. It will be found that soap solution made according to the directions given will require less than 20.5 cc., showing that it is too strong, and that dilution is necessary. Suppose only 17 cc. of the soap solution is required to produce a lather, and it is desired to dilute 200 cc., then each 17 cc. must be diluted to 20.5 cc.—that is, each 17 cc. must have 3.5 cc. (20.5—17) of the alcohol and

distilled water mixture added to obtain the correct strength. By proportion 200 cc. will require $\frac{200}{17} \times 3.5 = 41.2$ cc. to be added.

Process:

Total Hardness

100 cc. of the sample is placed in the stoppered bottle used in the standardisation test (after rinsing with distilled water), and standardised soap solution is added in the manner already described, until a persistent lather is obtained.

EXAMPLE :

100 cc. of the sample required 14.5 cc. of standard soap solution.

Then $14.5 - 0.5$ (for the lather) = 14 cc. required to precipitate the total hardness,

= 14 mgm. CaCO_3 in 100 cc. of the sample.

\therefore Total hardness = 14 parts per 100,000.

All hardness is calculated to the equivalent of calcium carbonate.

Permanent Hardness

100 cc. of the sample is boiled in a beaker to about 50 cc.; carbon dioxide is expelled and the temporary hardness is precipitated. The liquid is filtered through a small filter paper, and the paper is washed with successive quantities of freshly boiled distilled water until the filtrate measures 100 cc. This is made cold and titrated with the soap solution as before.

EXAMPLE :

100 cc. of the sample, treated as above, required 9 cc. standard soap solution.

Then $9 - 0.5 = 8.5$ cc. required to precipitate the permanent hardness, = 8.5 mgm. CaCO_3 in 100 cc. of the sample.

\therefore Permanent hardness = 8.5 parts per 100,000.

Temporary Hardness

By difference.

Total—permanent=temporary hardness.

EXAMPLE :

Figures as above.

$14 - 8.5 = 5.5$ parts per 100,000 temporary hardness.

As calcium carbonate is soluble in carbon-dioxide-free water, to the extent of three parts per 100,000, no attempt is made

to estimate the permanent and temporary hardness when the total does not exceed six parts per 100,000.

When the soap solution has been standardised against the standard hard water, and found too strong, it may be used without dilution if preferred, provided it is approximately correct and a correction is made in the calculation.

EXAMPLE :

20 cc. standard hard water=19 cc. soap solution. In a test this soap solution was used without diluting to correct strength, and it was found that 13.5 cc. was required to produce a lather with 100 cc. of a sample. Subtracting 0.5 cc. for the lather, the quantity of solution which would have been used had it been correct, would be

$$13.0 \times \frac{20.5}{19} = 14.0 \text{ cc.} = 14.0 \text{ parts hardness per 100,000.}$$

Similarly, if the soap solution is found to be under strength the calculation is made in the same way.

EXAMPLE :

20 cc. of standard hard water=23 cc. soap solution. In a test 7.0 cc. of this solution was required for 100 cc. of a sample. $6.5 \times \frac{20.5}{23} = 5.8$ cc. of correct strength would have been required to precipitate the hardness=5.8 parts hardness per 100,000.

IRON, LEAD, COPPER, AND ZINC

In the ordinary routine examination of water for metals it is only necessary to test for iron, lead, copper, and zinc. In rare instances the presence of arsenic, tin, chromium, manganese or other poisonous metals may be suspected, in which cases special processes for their detection and estimation will be employed.

Qualitative Examination

It is generally advisable first to concentrate the water by boiling 500 cc. to about 70 cc. after the addition of two drops of concentrated hydrochloric acid. If a precipitate forms on boiling, another drop or more of the acid is added, but just sufficient to keep the solids in solution; marked excess must be avoided. The concentrated liquid is cooled and used in the following tests, which are conveniently made in 10 cc. cylindrical measures; liquids in the glass are easily mixed by plunging in a glass rod having a flattened end.

About 10 cc. is taken, two drops of ammonium sulphide are

added (the ammonium sulphide must be fresh, as shown by the absence of colour in it) and the whole mixed. A dark coloration or precipitate indicates iron, lead, or copper, a cloudiness or white precipitate, the presence of zinc; the liquid is retained for a further test below if necessary. Iron, lead, or copper each give different shades of coloration: iron, a green tinge, except when present in large amount, and copper a browner coloration than lead. To distinguish between these three metals, about 0.5 cc. of 1 in 10 hydrochloric acid is added to a fresh 10 cc. portion of the concentrated water, mixed, and then two drops of ammonium sulphide as before; if no dark coloration is obtained now, iron is present, and lead and copper are absent. To distinguish between lead and copper, 0.5 cc. of 10 per cent. potassium cyanide is added to the liquid of the first test above and mixed; if the coloration disappears copper is present and lead is absent.

To confirm the presence of iron or copper, two drops of freshly prepared potassium ferrocyanide solution are added to a further portion; iron gives a blue, and copper a chocolate coloration. Zinc is confirmed by testing another portion; two drops of concentrated sulphuric acid are added, mixed, and then potassium ferrocyanide as in the foregoing; a white cloudiness or precipitate indicates zinc. We know of no really satisfactory confirmatory test for lead in water after concentration. Potassium dichromate solution, often advocated, is useless for this purpose except when the quantity of lead is sufficient to be detected by this test without concentration; a yellow cloudiness or precipitate is obtained.

Quantitative Examination

The quantitative determination of iron, lead, or copper is made by taking a definite volume of the sample and matching the colour produced by the addition of a reagent, with standards made with the same reagent, and containing known quantities of the metal. The water is concentrated or diluted, as may be necessary, so that the colour obtained is neither too faint nor too dark; the formation of a precipitate makes accurate matching impossible. The method of estimating zinc is on the same principle.

Iron

Iron is very commonly present in water, and its estimation is necessary only when the amount is excessive.

SOLUTIONS REQUIRED :

Standard Iron Solution. 1 cc.=1 mgm. iron.

1 gm. of pure iron wire is weighed into a beaker. After covering with a clock glass, dilute hydrochloric acid is added in small quantities at a time until solution is complete ; heating assists the reaction. Any liquid which has spirted on to the clock glass is washed into the beaker, the volume of the solution is made to about 200 cc., and 1 cc. of concentrated nitric acid is added. The whole is boiled for fifteen minutes, cooled, and made to 1 litre.

Ammonium Sulphide.

A solution of 1 part of strong ammonia with two parts of water is saturated with sulphuretted hydrogen.

PROCESS :

The water is concentrated after the addition of hydrochloric acid as may be necessary, or is diluted as required, to 100 cc. and the liquid placed in a measuring glass. Ammonium sulphide is added drop by drop until the maximum coloration is produced, and the whole is mixed by closing the open end of the glass with the palm of the hand and inverting two or three times. The colour is observed by looking down the column of liquid. Trials are then made with different 'standards' until a match is obtained. A 'standard' is made in the following manner: in another similar glass a definite volume of the standard solution is placed, this is made to 100 cc. with distilled water, ammonium sulphide is added as before, and the whole mixed.

EXAMPLE :

250 cc. of the sample was concentrated to 100 cc., and the colour obtained with ammonium sulphide was matched by a 'standard' containing 0.65 cc. standard iron solution. That is to say, the amount of iron in 250 cc. of the sample is equal to the quantity present in 0.65 cc. of the standard iron solution.

Now 1 cc. of the standard iron solution=1 mgm. iron.

∴ 0.65 cc.=0.65 mgm.

∴ 250 cc. of the sample contains 0.65 mgm. iron,

∴ 100 cc. contains 0.26 mgm.

Iron=0.26 parts per 100,000.

Lead and Copper

Lead and copper are estimated in the same way as iron, using the appropriate standard solution of the metal to be determined.

Standard Lead Solution. 1 cc.=1 mgm. lead.

1.8307 gm. of crystallised lead acetate is dissolved in a mixture of about 250 cc. distilled water and 5 cc. acetic acid; the whole is made to 1 litre.

Standard Copper Solution. 1 cc.=1 mgm. copper.

3.9281 gm. of crystallised copper sulphate is dissolved in water and made to 1 litre.

Zinc

The estimation of zinc, in the absence of iron, is carried out by a process similar to that already described, except that a match is made of the cloudiness produced on the addition of 1 cc. of a freshly prepared 10 per cent. solution of potassium ferrocyanide after adding 2 cc. of concentrated sulphuric acid.

Standard Zinc Solution

4.3987 gm. of crystallised zinc sulphate is dissolved in water and made to 1 litre.

The estimation of iron, lead, copper, and zinc as traces in water presents no difficulty when they are present singly; when in mixture, various modifications of methods will require to be adopted according to the large number of possible combinations. Very generally lead, copper, and zinc are not associated together, but each is commonly associated with iron.

Lead or copper may be estimated, in the presence of iron, by the method given, if 5 cc. of 1 in 10 hydrochloric acid is added previous to the addition of the ammonium sulphide. To estimate zinc associated with iron, it is separated by the following process :—

250 cc. of the sample with two drops (0.1 cc.) of concentrated sulphuric acid is boiled to about 100 cc. and made cold. 3 cc. of strong ammonia is now added and mixed; the iron is precipitated, and the zinc dissolves in the excess. The whole is filtered, the residue is washed, and the total filtrate boiled

to 50 cc. to remove ammonia. To the liquid when cold, 2 cc. of concentrated sulphuric acid is added, mixed, again cooled, and poured into a 100 cc. measuring cylinder; the beaker is washed with water into the measuring cylinder and the liquid is made to 100 cc., and then 2 cc. more water is added. The test then proceeds in the usual manner.

OXYGEN ABSORBED IN TWO HOURS AT 26-27° C. (80° F.)

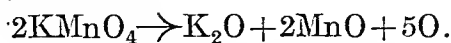
Modification of Forchammer's Process

This process has for its object the determination of the quantity of oxygen absorbed by any organic matter in the water, as some indication of the quantity of organic matter itself which is present. Many waters contain inorganic substances which are readily oxidised, such as ferrous salts, nitrites, and sulphuretted hydrogen, and in those cases, unless special steps are taken to eliminate the error, the oxygen-absorbed figure will be altogether too high. The process provides no information as to the origin and nature of the organic matter. Oxidation is not complete and the proportion oxidised varies within wide limits; much more accurate knowledge of the presence of organic matter is obtained from the free and albuminoid ammonia determination. The best that can be said for the oxygen-absorbed process is that it may furnish confirmatory evidence. It is given in full chiefly because it appears to be almost universally employed, though its actual value is such that it could be omitted without disadvantage. We discarded the process many years ago.

Reagents required:

Standard Potassium Permanganate Solution. 1 cc. = 0.1 mgm. oxygen.

Oxygen in potassium permanganate is available, in presence of sulphuric acid, as below:



Calculating from atomic weights, 316.06 parts of potassium permanganate furnish 80 parts of available oxygen by weight, \therefore 3.9507 gm. of potassium permanganate will furnish 1 gm. of oxygen, and if this quantity is dissolved in water and made

to 1 litre, 1 cc. of the solution = 1 mgm. oxygen. The above solution is diluted one in ten, then 1 cc. = 0.1 mgm. oxygen.

Sulphuric Acid.

25 per cent. solution to which potassium permanganate solution has been added until a minute trace of permanent pink colour is obtained.

Potassium Iodide, solid.

Starch Solution.

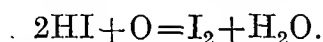
As indicator, preparation as on page 80.

Sodium Thiosulphate Solution.

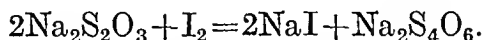
0.5 gm. pure sodium thiosulphate is dissolved in water and made to 500 cc. This is standardised in the process; it is prepared fresh each time it is required.

Process:

Two stoppered bottles of about 300 cc. capacity are required; these should not be used for any other purpose, and when not in use are kept filled with water made slightly acid with sulphuric acid. To one is added 100 cc. of the sample, and to the other 100 cc. of distilled water, and to each 10 cc. of sulphuric acid and 10 cc. of standard potassium permanganate solution. Both are placed in a water oven at 26 to 27° C. for two hours. At the end of this period a crystal of potassium iodide is added to each; iodine is set free by the available oxygen remaining.



Thiosulphate solution is then run into each bottle from a burette until the free iodine is removed, using starch solution as indicator.



The quantity of thiosulphate solution required is noted.

In titrating iodine with sodium thiosulphate solution, the latter is run in until the colour of the liquid is very faintly yellow, and only then is the starch solution (about 0.5 cc.) added; if the indicator is added when much free iodine is present a precipitate is formed which interferes with the accuracy of the titration. The titration is continued until the blue colour produced by the indicator is just discharged; the total quantity only of thiosulphate is noted. The rationale of the process is

as follows : In each bottle, at the beginning of the test, there is the same quantity of potassium permanganate solution, and therefore the same quantity of oxygen available, namely, 1 mgm. During the two hours any organic matter in the sample is oxidised (more or less), absorbing some of this oxygen. At the end of this period, whilst the distilled water contains the original amount, the sample contains only part. On addition of potassium iodide the available oxygen remaining in each liberates an equivalent quantity of iodine, and this free iodine requires a proportionate amount of thiosulphate solution to combine with it. The sample therefore requires less thiosulphate than the distilled water, and by calculation it is found how much oxygen this difference in thiosulphate solution represents.

EXAMPLE :

100 cc. of distilled water, and 100 cc. of sample were taken ; 10 cc. of standard potassium permanganate solution and 10 cc. of sulphuric acid were added to each. On titration, after standing for two hours at 26 to 27° C., it was found that the distilled water required 29.65 cc. of thiosulphate solution and the sample 24.20 cc. That is to say, the oxygen absorbed by the organic matter in the sample is equal to $29.65 - 24.20 = 5.45$ cc. of the thiosulphate solution.

Now 29.65 cc. of the thiosulphate solution = 10 cc. of permanganate solution = 1.0 mgm. oxygen ; \therefore 5.45 cc. of thiosulphate solution

$$= \frac{5.45}{29.65} \times 1.0 = 0.184 \text{ mgm. oxygen.}$$

\therefore 100 cc. of the sample, in two hours at 26 to 27° C., absorbs 0.184 mgm. oxygen = 0.184 parts per 100,000.

The time and temperature employed is not standard, and varies with different operators. It is the practice of some to bring the sample to a temperature of 26 to 27° C. before adding the permanganate solution and sulphuric acid, the time of standing counting from the moment the permanganate solution is added. Some chemists prefer to determine the oxygen absorbed in fifteen minutes and that absorbed in four hours, the amount absorbed in the shorter time being considered mainly due to animal, and the increase in the latter to vegetable, matter.

It is important that the liquids stand in the dark, as much higher results are obtained if exposed to light. An excess of oxygen, as shown by a distinct pink colour, must always be present ; if the colour becomes nearly discharged, a further

10 cc. or more permanganate solution is added, due allowance being made for this in the calculation.

PHOSPHATES

Tests for phosphates in water are very rarely necessary.

Reagents required:

Hydrochloric Acid, concentrated.

Ammonium Molybdate Solution.

20 gm. of ammonium molybdate is dissolved in a mixture of 60 cc. of water and 25 cc. liquor ammonia. This solution is added in small quantities at a time, with stirring after each addition, to 250 cc. of a mixture containing equal parts of concentrated nitric acid and water. The whole is allowed to stand for a fortnight and then the clear solution is decanted from the precipitate which forms.

Nitric Acid, concentrated.

Process:

100 cc. of the water is concentrated to about 20 cc., after the addition of two drops of concentrated hydrochloric acid. 2 cc. of concentrated nitric acid is added, and, after the liquid has been heated to nearly boiling, about 1 cc. of ammonium molybdate solution. The whole is allowed to stand in a warm place for about ten minutes. The presence of phosphates is indicated by the formation of a yellow colour, cloudiness, or precipitate, according to the quantity present. If a positive result is obtained it is advisable to repeat the test after removing any silica which may be present, as this substance responds to the same test. For this purpose the water is evaporated to dryness in a *porcelain* basin, and the residue, after the addition of 3 cc. of concentrated hydrochloric acid, is heated on a hot plate for one hour to render the silica insoluble. The residue is taken up with dilute nitric acid, filtered, and the filtrate tested as described above. A control test with distilled water is essential in each case.

SULPHATES

The estimation of sulphates in water is only necessary when their presence in excessive amount is indicated.

Process:

500 cc. of the water, to which 2 cc. of concentrated hydrochloric acid has been added, is boiled in a beaker to about 300 cc. The burner is removed, and 5 to 10 cc. of a 5 per cent. solution of barium chloride is added; the sulphates are precipitated as barium sulphate.

Gentle boiling is recommenced and continued for at least one hour, and then the whole is filtered through a filter paper which retains very fine precipitates, and which gives a negligible ash. The beaker is thoroughly washed out with boiling distilled water, and any solid adhering is removed by rubbing with a glass rod tipped with a piece of rubber tubing. The precipitate, having been completely transferred to the filter paper, is washed until the filtrate gives no reaction with silver nitrate solution, showing absence of chlorides. The filter paper with its contents is then placed in a weighed platinum crucible and ignited. The paper is completely burned away, and after cooling the crucible, the residue is moistened with dilute sulphuric acid, reignited, cooled, and weighed again; the increase in weight gives the amount of sulphates as barium sulphate. A second ignition and weighing is necessary to make sure that incineration is complete.

EXAMPLE:

500 cc. of water, treated as above, yielded 0.1432 gm. of BaSO_4 .

Now BaSO_4 is to SO_3 as 233.43 is to 80.06, therefore to calculate the BaSO_4 to SO_3 the quantity is multiplied by 0.3430.

$$0.1432 \text{ gm.} \times 0.3430 = 0.0491 \text{ gm. } \text{SO}_3 \text{ in 500 cc.}$$

$$= 0.0098 \text{ gm. in 100 cc.}$$

$$= 9.8 \text{ mgm. in 100 cc.}$$

$$\therefore \text{SO}_3 = 9.8 \text{ parts per 100,000.}$$

DISSOLVED OXYGEN

Though not included in the routine examination of water, the estimation of the dissolved oxygen is occasionally of value; the most convenient method is that of Winkler.

Solutions required:*Manganous Chloride.*

33 gm. of the crystallised salt is dissolved in water and made to 100 cc.

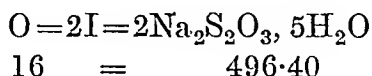
Potassium Hydroxide and Potassium Iodide.

70 gm. of potassium hydroxide and 10 gm. of potassium iodide are dissolved together in water and made to 100 cc.

Hydrochloric Acid, concentrated.

Standard Sodium Thiosulphate. 4.4460 gm. per litre, 1 cc.
= 0.1 cc. oxygen.

One atom of oxygen liberates two atoms of iodine, and this reacts with two molecules of sodium thiosulphate. This may be stated thus :

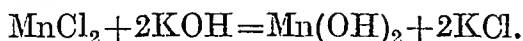


That is to say, 16 gm. of oxygen is equivalent to 496.40 gm. of crystallised sodium thiosulphate. Now the molecular weight of any gas, in grammes, occupies 22.33 litres at N.T.P., therefore the atomic weight of oxygen (16) occupies half this volume = 11.165 litres. Therefore 496.40 gm. of crystallised sodium thiosulphate = 11.165 litres of oxygen—that is, 4.4460 gm. = 0.1 litre of oxygen, and if this quantity of sodium thiosulphate is dissolved in water and made to 1 litre, 1 cc. of the solution will equal 0.1 cc. oxygen.

Starch Solution, as indicator (page 80).

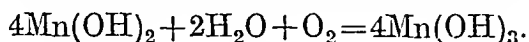
Process :

The temperature of the water is taken, and then a well-stoppered bottle of exactly known capacity, about 350 cc., is quite filled with the sample, by syphonage or other means which will prevent artificial aeration. 1 cc. of manganous chloride and 4 cc. of the potassium hydroxide and potassium iodide solution are added from pipettes placed as far down in the bottle as possible: Manganous hydroxide is precipitated according to the following equation :

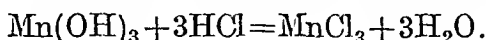


The stopper is inserted and the bottle, held by the neck to prevent heating of the liquid, is inverted several times to allow the precipitate to mix thoroughly. The manganous hydroxide

takes up the dissolved oxygen in the water, and forms manganic hydroxide in proportion to the quantity of oxygen present.



The bottle is stood in a dark place for fifteen minutes to allow the precipitate to settle, and then 5 cc. of concentrated hydrochloric acid is added from a pipette in the manner already described. The manganic hydroxide forms manganic chloride.



The manganic chloride liberates an equivalent amount of iodine from the second reagent added.



The whole liquid is then poured into a beaker and titrated with the standard sodium thiosulphate solution, using starch indicator, and the quantity required to combine with the free iodine is noted.

EXAMPLE :

Temperature of water, 14° C. Capacity of bottle, 354 cc.

On titration 14.2 cc. of standard sodium thiosulphate solution was required.

No appreciable error is introduced by neglecting the volume of sample displaced by the addition of reagents.

Now 1 cc. of the thiosulphate solution = 0.1 cc. of oxygen.

∴ 14.2 cc. " " " = 1.42 cc. "

∴ 354 cc. of the sample contains = 1.42 cc. "

∴ 1000 cc. " " " 4.01 cc. "

∴ This sample at 14° C. contains 4.01 cc. of dissolved oxygen per litre.

The presence of nitrites vitiates the test, and the originator of the process later described a modification to eliminate error in such cases.¹

SILICA AND 'INSOLUBLE,' IRON, ALUMINIUM, CALCIUM, AND MAGNESIUM

Occasionally further information as to the composition of the total solids in water is required, and then a gravimetric estimation is made of silica and 'insoluble,' iron, aluminium, calcium, and magnesium.

¹ Winkler, *Zeitsch. angew. Chem.*, 1916, 29, pp. 44-46.

5 litres of the sample is acidified with dilute hydrochloric acid and boiled to small bulk; the concentrated liquid is transferred to a small porcelain basin and evaporated to dryness. To the residue 5 cc. of concentrated hydrochloric acid is added; the whole is then evaporated on a hot plate and afterwards baked for two hours. The residue is taken up with dilute (2 per cent.) hydrochloric acid, filtered, and washed. The residue of *silica and insoluble* from filtration is ignited, preferably in a platinum crucible, and weighed until constant.

The filtrate is boiled to small bulk after the addition of three drops of concentrated nitric acid, slight excess of ammonia is then added, and the whole boiled until no smell of ammonia is apparent; the precipitate of *iron and aluminium* hydroxides is filtered off, washed, ignited, and weighed (as oxide) as before.

The quantity of iron found colorimetrically (page 90) is calculated to *ferric oxide*, Fe_2O_3 , by multiplication with the factor 1.4298, and this, subtracted from the total oxides above, gives *alumina*, Al_2O_3 .

To the filtrate slight excess of ammonium oxalate is added, and the whole boiled for at least half an hour, filtered, washed, and the precipitate of calcium oxalate is ignited as before. The calcium is weighed as *calcium oxide*, CaO ; strong ignition is required to make the conversion to oxide complete.

The filtrate is boiled to small bulk, made quite cold, 20 cc. of strong ammonia is added, and then slight excess of sodium phosphate solution; after thorough mixing the whole is allowed to stand overnight. The precipitate of phosphate is filtered, washed in the cold with ammonia (1 in 3), ignited, and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$; factor for calculating to *magnesium oxide*, MgO , $\times 0.3621$.

In each case the results are calculated to parts per 100,000. The filter papers must be of the best quality for retention of fine precipitates, and yielding a negligible ash.

INTERPRETATION OF RESULTS

As already stated, a sanitary water analysis has for its chief object the detection of sewage pollution, as a latent or active carrier of pathogenic organisms, and any dissolved matter which would prove injurious to health.

In most analytical work, the expression of an opinion as to the quality or suitability of a sample, only requires a comparison of the analytical data found with fixed standards or specifications. Sanitary water analysis, however, is an exception, and considerable knowledge must be gained before it is possible to arrive at proper conclusions regarding the significance of the various figures. Definite standards cannot be promulgated, and each result must be considered in the light of all the other figures; the import of the whole depends on the source and specific history of the sample.

It cannot be urged too strongly that it is rarely possible to give a correct opinion on a sample of water without a full knowledge of the source of supply. The analyst must remember that he or she is only dealing with a *sample*, and that caution is advisable when pronouncing an opinion regarding the *supply*.

The term 'animal matter' which occurs in the succeeding pages is used to distinguish it from 'vegetable matter'; it denotes substances of excretal origin, and includes material from both animal and human sources. Chemical analysis does not differentiate between the latter.

Reaction

Most waters are faintly alkaline, due to the calcium, magnesium, and sodium salts contained in them. An acid reaction may be due to humic and other vegetable acids, or to an excessive quantity of carbon dioxide; a change to neutral or alkaline after heating the water would indicate the latter cause. The reaction is not of great importance, except that an acid water may be found to have a marked action on metals.

Odour

The presence of an odour in water generally indicates some

contamination. A perceptible odour can be imparted by the entry of innumerable substances, but it is most frequently due to the growth of certain algae, which are generally themselves harmless, or to bacteria. Contamination with sewage may cause water to have an odour, but only when the pollution is gross. Some otherwise pure waters have an odour of sulphuretted hydrogen.

Colour

A markedly coloured water has an objectionable appearance, but often such a water is otherwise good. The purest waters are without any colour, or with just a faint tinge of blue or green. A colour may be due to the presence of substances of either vegetable, mineral, or animal origin, and when very noticeable an endeavour should be made to discover its nature. Peaty waters invariably have a marked colour.

Clarity or Turbidity

It is desirable that a water should be clear, though generally any turbidity is due to substances which on examination are found to be in themselves harmless. Water containing iron may be clear when drawn, and become turbid on standing in the air. When the water in a well is normally clear but becomes turbid after heavy rain, it is an indication of possible pollution.

Taste

Good water is pleasant to the taste, but has no appreciable flavour. The presence of an excessive quantity of iron, sodium chloride, or peat may give water a perceptible taste.

Total Solids, Non-Volatile Solids, Volatile Solids, Solids in Suspension

Waters vary largely in their solid content, and, speaking generally, the less solid matter a water contains the more suitable it is for drinking and domestic purposes. The total solids should not exceed 50 parts per 100,000, and, if in excess of this quantity, the permissible amount must depend largely on their composition.

The sum-total of the chlorine calculated as sodium chloride,

hardness and nitrates, should very approximately equal that of the non-volatile solids; if there is a discrepancy, some undetermined constituent, generally sodium carbonate or sodium sulphate, is present.

The volatile solids are, to a large extent, of an organic nature, and should be low, though that of vegetable origin has little significance. A considerable amount of organic matter is indicated by charring on ignition of the total solid residue.

The estimation of the solids provides no real information as to the presence of animal contamination of the water. Solids in suspension should be absent.

Chlorine as Chlorides

Chlorine as chlorides is present in all natural waters, chiefly as sodium chloride, and may be derived from both harmless and harmful sources.

In contact with strata, water takes up chlorides in varying degree, from traces which are harmless, to enormous amounts sufficient to render the water entirely inadmissible for drinking. In the neighbourhood of the sea, chlorine may amount to fifteen parts or more per 100,000, and yet have no significance. The use of hypochlorites for the sterilisation of water results in only a negligible addition to the chlorine content, as the proportion employed is very small.

Pollution with sea-water, urine, and much more rarely, with certain trade effluents, causes an addition of a large amount of chlorine. If sea-water has gained access a high figure for magnesia will be obtained; animal pollution will be indicated by the tests for free ammonia, nitrites, and nitrates; and the entry of trade effluents is likely to be revealed by the presence of some abnormal constituent. As an indicator of sewage contamination the chlorine figure is not of much value, as sewage itself only contains an average of about 11 parts of chlorine per 100,000. Vegetable matter contains little or no chlorine.

Provided that chlorine is derived from harmless sources and is chiefly in the form of sodium chloride, a permissible limit is 40 parts of chlorine per 100,000.

Free Ammonia, Albuminoid Ammonia, Nitrites, Nitrates

The determinations free ammonia, albuminoid ammonia, nitrites, and nitrates are the most important tests in a sanitary water analysis, as they provide the chief indications of animal contamination. These substances are all so closely related that their significance may be conveniently considered together. When present in excessive amount they very frequently have a harmful origin, but they may also be derived from entirely innocuous sources; in deciding their derivation in such cases the analyst is guided to a large extent by a knowledge of the supply.

Animal matter is rich in nitrogen, and when present in water decomposes. The first product of the decomposition is free ammonia, and this is oxidised by nitrifying organisms to nitrites, and finally to nitrates. The process is one of natural purification, and may be considered chemically complete when nitrates alone are present. A high figure for nitrates derived from animal matter is in itself a warning of potential danger, for at some future time, owing to excessive rainfall or other cause, the organisms responsible for the purification process may be unable to deal efficiently with the increased volume. Nitrites oxidise rapidly, and if the analysis has been delayed, it is possible for a polluted water to be found free from nitrites; on the other hand, if pollution is very recent, a low nitrates figure may be obtained, because sufficient time has not elapsed for their production in quantity. Plant life removes nitrates from water. With limitations, which are discussed later, it can be stated very broadly that free ammonia and nitrites indicate recent contamination, and nitrates past contamination.

Vegetable matter does not decompose in this manner, and yields practically no free ammonia, nitrites, or nitrates (the quantities are so small as to be negligible), but the nitrogen is more or less completely obtained as albuminoid ammonia. Organic matter of animal origin yields less albuminoid ammonia than free ammonia.

If a water does not contain more than 0.004 parts of free ammonia, 0.008 parts of albuminoid ammonia, and 0.15 parts of nitrates per 100,000, and nitrites are not present, it can be

accepted that animal contamination is absent. If these quantities are exceeded it is necessary to decide whether they are derived from harmful or harmless sources.

Rain-water may contain as much as 0.070 parts of free ammonia per 100,000, and a small amount of nitrites derived from the atmosphere, the quantities depending on the purity of the air in the neighbourhood where the rain has fallen. Distilled water may contain a large amount of free ammonia, according to the purity of the water from which it has been prepared. Nitrates in water may be reduced to nitrites and to ammonia, by ferrous salts in the strata, which act as reducing agents; the same action may take place if the water traverses long lengths of metal pipes or is stored in metal tanks. If this has occurred a minute trace of metal will probably be found in the water. Again, nitrates in water may be derived from strata rich in nitrates (*e.g.* chalk, oolite) with which it has been in contact, but such a water, if unpolluted, will, in normal circumstances, contain little free ammonia and no nitrites.

High free ammonia and nitrates, and presence of nitrites in water from a shallow well, almost certainly indicates dangerous contamination; in a deep well these constituents may be high and yet have no significance.

Peaty water may yield as much as 0.1 parts of albuminoid ammonia per 100,000 derived entirely from harmless vegetable matter, but the water will have an unpleasant appearance.

With the reservations already discussed, the question may be summarised thus: High free ammonia with comparatively high albuminoid ammonia, the presence of nitrites and high nitrates indicates animal pollution; low free ammonia with high albuminoid ammonia, absence of nitrites and low nitrates indicates vegetable contamination; low free ammonia with comparatively high albuminoid ammonia, absence of nitrites and high nitrates indicates residue from animal pollution after natural purification.

Oxygen absorbed in Two Hours at 26 to 27° C. (80° F.)

Little reliance can be placed on the results obtained with this test; in the description of the process its many grave

defects have been pointed out. A high result is not at all necessarily indicative of dangerous contamination, but if the figure is less than 0.06 parts per 100,000 this may provide some confirmatory evidence of the purity of a water. The vegetable matter in a peaty water may absorb as much as 3.0 parts per 100,000.

Hardness

The hardness, unless it is extremely excessive, does not affect the quality of water for drinking, but it is of prime importance in considering the suitability for general domestic purposes.

From this point of view the most satisfactory water is that containing 4 to 5 parts of total hardness per 100,000. The hardness should not exceed 30 parts per 100,000, though several public supplies contain considerably more than this. With soft water (less than 3.0 parts per 100,000) an action on metals may take place.

The hardness of the water in the neighbourhood does not appear to have any bearing on the general health of the community.

Iron

The presence of iron is of common occurrence. Frequently it is in the form of ferrous bicarbonate and, on exposure to air, the unstable salt loses carbon dioxide and ferrous carbonate is precipitated; this rapidly oxidises to ferric carbonate, producing, if the iron is in sufficient quantity, an opalescence. Iron should not exceed 0.35 parts per 100,000.

Lead

Highly oxygenated waters have a marked solvent action on lead, with the formation of lead hydroxide. If carbon dioxide is present, the lead may be precipitated as lead carbonate; in presence of an excess of carbon dioxide soluble lead bicarbonate is formed, and the lead remains in solution. Other waters which are considered to have an action on lead are acid waters (*e.g.* peaty), very soft waters, and those containing an appreciable quantity of ammonium salts, particularly the nitrate. The presence of phosphates

diminishes the plumbo-solvent action very considerably. Lead must certainly not exceed 0.05 parts per 100,000, and no supply can be considered really satisfactory if it contains any at all.

Copper

The presence of copper in a natural water is extremely uncommon ; it must not exceed 0.07 parts per 100,000.

Zinc

The increasing use of zinc and galvanised iron for pipes and cisterns accounts for the great frequency in which this metal, generally as bicarbonate, is found in water. It occurs naturally as sulphate in a few waters. Zinc in potable waters is rarely present in sufficient quantity to produce harmful results. Thresh¹ records the case of a small community of all ages who for ten years had used no other water than one containing 0.49 to 1.12 parts of zinc per 100,000 without any ill effect. Again, Scott and Jameson² reported that during a period of two years a depot of some 200 men had as its sole supply a water containing 2.50 to 4.72 parts per 100,000, and no disturbance of health resulted.

Sulphates

The significance of sulphates depends to a large extent on the base with which they are combined. Sodium or magnesium sulphate should not be present in amount exceeding 20 parts per 100,000, calculated as Na_2SO_4 .

Phosphates

Phosphates are seldom found in water, as they are readily removed from solution by various agencies, consequently their absence has no significance. When present they are generally derived from excreta, and may provide confirmatory evidence of animal contamination, but they can also have their origin in strata, and their presence may have no dangerous indication.

¹ *Lancet*, 1915, vol. ii.

² *Ibid.*, 1917, vol. i.

Dissolved Oxygen

This estimation is occasionally of value, particularly in the case of a river water, to determine how much oxygen has been consumed in oxidising impurities, or is present in solution and available for this purpose. At ordinary temperature the amount of dissolved oxygen present should not be less than 4.0 cc. per litre. Water saturated with air contains 8.68 cc. of oxygen per litre at 5° C.; 7.77 cc. at 10° C.; 6.96 cc. at 15° C.; and 6.28 cc. at 20° C.

TYPICAL ANALYSES

In the following pages we give some typical analyses to illustrate the interpretation of water analysis results. The reports are taken from our laboratory journals, and notes have been appended.

No. 1.—Upland surface water. Supply of a large town in Devon, taken from tap in house.

Total Solids	. . .	4.80	} parts per 100,000.
Non-Volatile Solids	. . .	3.00	
Volatile Solids	. . .	1.80	
Suspended Solids	. . .	Small quantity	
Free and Saline Ammonia	. . .	0.0010	
Albuminoid Ammonia	. . .	0.0088	
Nitrous Nitrogen (Nitrites)	. . .	Absent	
Nitric Nitrogen (Nitrates)	. . .	0.016	
Total Hardness	. . .	1.70	
Temporary Hardness	. . .	—	
Permanent Hardness	. . .	—	
Chlorine (Chlorides)	. . .	1.10	
Iron, Lead, Copper, Zinc	. . .	Trace of Iron	
Reaction	Neutral to litmus.	
Colour	Moderately good.	
Clarity or Turbidity	Clear.	
Odour	None.	

Remarks.—The chemical analysis of this sample indicates a water of very good quality.

No. 2.—Deep well water, supply of town in Dorset. Taken from household tap. Strata: chalk. No known source of pollution.

Total Solids . . .	28.00	} parts per 100,000.
Non-Volatile Solids . .	24.50	
Volatile Solids . . .	3.50	
Suspended Solids . . .	Nil	
Free and Saline Ammonia ..	0.0004	
Albuminoid Ammonia . .	0.0080	
Nitrous Nitrogen (Nitrites) .	Absent	
Nitric Nitrogen (Nitrates) .	0.368	
Total Hardness . . .	23.00	
Temporary Hardness . .	16.00	
Permanent Hardness . .	7.00	
Chlorine (Chlorides) . .	1.60	}
Iron, Lead, Copper, Zinc .	Absent	
Reaction	Faintly alkaline to litmus.	
Colour	Very good.	
Clarity or Turbidity . .	Quite clear.	
Odour	None.	

Remarks.—The chemical analysis of this sample indicates a water of good quality. It is rather hard.

No. 3.—Well in Yorkshire, 175 feet deep, tubed 100 feet. Strata: superficial formation, 56 feet; grey and green sand, 74 feet; red sandstone, 45 feet. Possible sources of pollution, rain-water tank, 40 feet deep, adjoining well.

Total Solids . . .	72.00	} parts per 100,000.
Non-Volatile Solids . .	65.00	
Volatile Solids . . .	7.00	
Suspended Solids . . .	Large quantity	
Free and Saline Ammonia .	0.0750	
Albuminoid Ammonia . .	0.0068	
Nitrous Nitrogen (Nitrites) .	Very faint trace	
Nitric Nitrogen (Nitrates) .	Trace	
Total Hardness . . .	32.50	
Temporary hardness . .	27.00	
Permanent hardness . .	5.50	}
Chlorine (Chlorides) . .	2.80	
Iron, Lead, Copper, Zine .	Iron present in large quantity.	

Reaction	Alkaline to litmus.
Colour	Marked.
Clarity or Turbidity	Cloudy.
Odour	None.

Remarks.—The chemical analysis of this sample indicates a water which can be passed as fit for potable purposes. There is, however, a considerable quantity of matter in suspension, and the removal of this would cause a great reduction in the amount of iron. It is very hard.

Notes.—This is a typical greensand water. The high free ammonia figure and the presence of nitrites is due to the reduction of nitrates by the ferrous salts in the strata. The cloudiness is due to the iron present.

No. 4.—Tube well in Norfolk, 200 feet deep. Strata: 100 feet clay, and then chalk for an unknown depth. Possible sources of pollution, stable and cattle sheds about 300 yards away.

Total Solids	55.00	} parts per 100,000.
Non-Volatile Solids	52.00	
Volatile Solids	3.00	
Suspended Solids	Nil	
Free and Saline Ammonia	0.0020	
Albuminoid Ammonia	0.0090	
Nitrous Nitrogen (Nitrites)	Absent	
Nitric Nitrogen (Nitrates)	0.012	
Total Hardness	43.60	
Temporary Hardness	37.30	
Permanent Hardness	6.30	
Chlorine (Chlorides)	2.35	
Iron, Lead, Copper, Zinc	Trace of Iron	
Reaction	Faintly alkaline to litmus	
Colour	Good.	
Clarity or Turbidity	Some cloudiness.	
Odour	None.	

Remarks.—The chemical analysis of this sample indicates a water which can be passed as fit for potable purposes. It is excessively hard.

Notes.—This water, being derived from chalk, contains a large amount of temporary hardness.

No. 5.—Supply of town in central France. Artesian well about 600 feet deep. Strata: chalk, clay, sand, and flint. No known possible source of pollution.

Total Solids	. . .	35.20	} parts per 100,000.
Non-Volatile Solids	. . .	31.20	
Volatile Solids	. . .	4.00	
Suspended Solids	. . .	Considerable quantity	
Free and Saline Ammonia	. . .	0.0014	
Albuminoid Ammonia	. . .	0.0077	
Nitrous Nitrogen (Nitrites)	. . .	Absent	
Nitric Nitrogen (Nitrates)	. . .	0.024	
Total Hardness	. . .	18.94	
Temporary Hardness	. . .	14.71	
Permanent Hardness	. . .	4.23	
Chlorine (Chlorides)	. . .	2.10	
Iron, Lead, Copper, Zinc	. . .	Iron present	
Reaction	. . .	Alkaline to litmus.	
Colour	. . .	Good.	
Clarity or Turbidity	. . .	Some cloudiness.	
Odour	. . .	None.	

Remarks.—The chemical analysis of this sample indicates a water of good quality.

Notes.—The sample was taken direct from the well and is filtered before delivery to the service mains.

No. 6.—Piped borehole in Aberdeenshire, 18 feet deep. Strata: clay, sand, and granite rock. No known possible source of pollution.

Total Solids	. . .	39.80	} parts per 100,000.
Non-Volatile Solids	. . .	32.80	
Volatile Solids	. . .	7.00	
Suspended Solids	. . .	Large quantity	
Free and Saline Ammonia	. . .	0.0026	
Albuminoid Ammonia	. . .	0.0034	
Nitrous Nitrogen (Nitrites)	. . .	Absent	
Nitric Nitrogen (Nitrates)	. . .	Trace	
Total Hardness	. . .	14.00	
Temporary Hardness	. . .	4.50	
Permanent Hardness	. . .	9.50	

Chlorine (Chlorides)	2.05 parts per 100,000.
Iron, Lead, Copper, Zinc	Iron present in large quantity.

Reaction	Neutral to litmus.
Colour	Marked.
Clarity or Turbidity	Turbid.
Odour	None..

Remarks.—The chemical analysis of this sample indicates a water that can be passed as fit for potable purposes. Doubtless the appearance of the water will improve when the well has been in use for some time.

Notes.—The above figures show the water in this shallow well to be free from organic contamination, and the presence of inorganic suspended matter is without significance in view of the fact that the construction of the borehole had just been completed.

No. 7.—Well in Yorkshire, 16 feet deep. Strata: clay and marl. Possible sources of pollution, no information.

Total Solids	132.20	} parts per 100,000.
Non-Volatile Solids	99.60	
Volatile Solids	32.60	
Suspended Solids	Small quantity	
Free and Saline Ammonia	0.0070	
Albuminoid Ammonia	0.0154	
Nitrous Nitrogen (Nitrites)	Absent	
Nitric Nitrogen (Nitrates)	3.603	
Total Hardness	46.97	
Temporary Hardness	15.11	
Permanent Hardness	31.86	
Chlorine (Chlorides)	11.70	
Iron, Lead, Copper, Zinc	{ Zinc, 1.80 Iron, trace	
Reaction	Alkaline to litmus.	
Colour	Indifferent.	
Clarity or Turbidity	Clear.	
Odour	None.	

Remarks.—The chemical analysis of this sample indicates a water which has been polluted in the past with animal matter and that a process of natural purification has not been complete. The solids

in solution and hardness are excessive; a marked quantity of zinc is present.

Notes.—The nitrates are abnormal, and indications point to their being derived from previous excretal contamination; that the process of natural purification has not been complete is shown by the rather high free ammonia figure. Subsequent inquiries elicited the information that the water-pipes were galvanised iron; it is probable that the solvent action of this water on zinc is due to the abnormal quantity of nitrates.

No. 8.—Spring well, 40 feet deep on island in the English Channel.

Strata of island: sand and rock. No known possible source of pollution.

Total Solids	. . .	42.00	} parts per 100,000.
Non-Volatile Solids	. . .	33.50	
Volatile Solids	. . .	8.50	
Suspended Solids	. . .	Considerable quantity	
Free and Saline Ammonia	. . .	0.0084	
Albuminoid Ammonia	. . .	0.0456	
Nitrous Nitrogen (Nitrites)	. . .	Absent	
Nitric Nitrogen (Nitrates)	. . .	0.410	
Total Hardness	. . .	9.47	
Temporary Hardness	. . .	1.66	
Permanent Hardness	. . .	7.81	
Chlorine (Chlorides)	. . .	15.20	}
Iron, Lead, Copper, Zinc	. . .	Trace of Iron	
Reaction	. . .	Neutral to litmus.	
Colour	. . .	Marked.	
Clarity or Turbidity	. . .	Some cloudiness.	
Odour	. . .	None.	

Remarks.—The chemical analysis of this sample indicates a water which is almost certainly contaminated with animal matter, and the doubtful purity renders it unsafe for potable purposes. An examination of the site should be made by a properly qualified person.

Notes.—The comparatively high free ammonia, high albuminoid ammonia, and the high nitrate figures are the chief factors in causing suspicion of this water. If nitrites were present there would be no doubt that pollution had occurred. The excessive chlorine is chiefly due to the proximity of the sea, but part may be derived from excreta.

No. 9.—Spring in Devon, piped and adequately protected.
Strata of district, slate. Possible sources of pollution
not known.

Total Solids	. . .	41.20	} parts per 100,000.
Non-Volatile Solids	. . .	27.60	
Volatile Solids	. . .	13.60	
Suspended Solids	. . .	Nil	
Free and Saline Ammonia	. . .	Absent	
Albuminoid Ammonia	. . .	0.0028	
Nitrous Nitrogen (Nitrites)	. . .	Absent	
Nitric Nitrogen (Nitrates)	. . .	0.400	
Total Hardness	. . .	20.00	
Temporary Hardness	. . .	5.13	
Permanent Hardness	. . .	14.87	
Chlorine (Chlorides)	. . .	10.60	}
Iron, Lead, Copper, Zinc	. . .	Absent	
Reaction	Faintly alkaline to litmus.	
Colour	Good.	
Clarity	Quite clear.	
Odour	None.	

Remarks.—The chemical analysis of this sample indicates a water of good quality.

Notes.—The chlorine figure is high, but is without significance. The above is a report on the tenth examination of this water; nine other samples, taken at irregular intervals and after various weather conditions, over a period of four years, have been examined, and similar results were obtained in each case. There is a history of a sea-water swimming-bath being allowed, several years ago, to empty into the surrounding strata.

No. 10.—Spring in Ross-shire, coming from the wooded slope of a small plateau the top of which is under cultivation.
No possible sources of pollution known.

Total Solids	. . .	26.00	} parts per 100,000.
Non-Volatile Solids	. . .	15.00	
Volatile Solids	. . .	11.00	
Suspended Solids	. . .	Nil	
Free and Saline Ammonia	. . .	0.0096	
Albuminoid Ammonia	. . .	0.0320	
Nitrous Nitrogen (Nitrites)	. . .	Present	

Nitric Nitrogen (Nitrates)	. 0.888	} parts per 100,000.
Total Hardness	. 8.96	
Temporary Hardness	. Nil	
Permanent Hardness	. 8.96	
Chlorine (Chlorides)	. 2.65	
Iron, Lead, Copper, Zinc	. Absent	

Reaction	. Faintly alkaline to litmus.
Colour	. Good.
Clarity or Turbidity	. Quite clear.
Odour	. None.

Remarks.—The chemical analysis of this sample indicates a water contaminated with animal matter of excretal origin.

Notes.—The indications of pollution are distinctly present, and there is no reason to believe that they have a harmless origin.

No. 11.—A shallow stream in Argyllshire. Strata of district: rock, peat, and moss-land. Possible sources of pollution, none known.

Total Solids	. 19.10	} parts per 100,000.
Non-Volatile Solids	. 14.60	
Volatile Solids	. 4.50	
Suspended Solids	. Considerable quantity	
Free and Saline Ammonia	. 0.0012	
Albuminoid Ammonia	. 0.0132	
Nitrous Nitrogen (Nitrites)	. Absent	
Nitric Nitrogen (Nitrates)	. Trace	
Total Hardness	. 8.82	
Temporary Hardness	. 1.40	
Permanent Hardness	. 7.42	
Chlorine (Chlorides)	. 2.80	
Iron, Lead, Copper, Zinc	. Absent	
Reaction	. Faintly alkaline to litmus.	
Colour	. Indifferent.	
Clarity or Turbidity	. Slight cloudiness.	
Odour	. None	

Remarks.—The chemical analysis of this sample indicates a water free from animal contamination; it is obvious that, unless adequately protected, the supply will be open to pollution of the grossest kind

No. 12.—Loch in Inverness. Strata of district : peat and sand.

Total Solids	12.15	} parts per 100,000.
Non-Volatile Solids	6.35	
Volatile Solids	5.80	
Suspended Solids	Large quantity	
Free and Saline Ammonia	0.0052	
Albuminoid Ammonia	0.0300	
Nitrous Nitrogen (Nitrites)	Absent	
Nitric Nitrogen (Nitrates)	Trace	
Total Hardness	6.13	
Temporary Hardness	—	
Permanent Hardness	—	
Chlorine (Chlorides)	1.70	
Iron, Lead, Copper, Zinc	Absent	
Reaction	Neutral to litmus.	
Colour	Very dark brown.	
Clarity or Turbidity	Almost opaque in 1-ft. tube.	
Odour	None	

Remarks.—The chemical analysis of this sample reveals no evidence of dangerous pollution, but the water contains a large amount of peat.

Notes.—The high albuminoid ammonia is characteristic of a peaty water.

No. 13.—Distilled water for drinking, prepared on board ship from sea-water. Sample taken direct from delivery pipe.

Total Solids	7.64	} parts per 100,000.
Non-Volatile Solids	5.80	
Volatile Solids	1.84	
Suspended Solids	Nil	
Free and Saline Ammonia	0.0055	
Albuminoid Ammonia	0.0012	
Nitrous Nitrogen (Nitrites)	Absent	
Nitric Nitrogen (Nitrates)	Trace	
Total Hardness	4.20	
Temporary Hardness	—	
Permanent Hardness	—	
Chlorine (Chlorides)	3.95	
Iron, Lead, Copper, Zinc	{ Lead, 0.107 Copper, 0.140 }	

Reaction	Faintly acid to litmus.
Colour	Good.
Clarity or Turbidity . .	Quite clear.
Odour	Faint smell of oil.

Remarks.—This sample of water contains lead and copper in sufficient quantity to condemn the water for potable use. A trace of sea-water appears to have gained access, and there is also some contamination with oil.

Notes.—It is to be noted that this water, which has dissolved lead and copper, has a faint acid reaction. The contamination with sea-water cannot be great, as sea-water contains about 1890 parts of chlorine per 100,000. The presence of oil in water distilled in large quantity is a comparatively common occurrence. (Compare with No. 14.)

No. 14.—Same source as No. 13, three months later, after rectification of defects in distilling plant.

Total Solids	2.00	} parts per 100,000.
Non-Volatile Solids . .	1.20	
Volatile Solids	0.80	
Suspended Solids . . .	Nil	
Free and Saline Ammonia .	0.0033	
Albuminoid Ammonia . .	0.0042	
Nitrous Nitrogen (Nitrites)	Absent	
Nitric Nitrogen (Nitrates)	Faint trace	
Total Hardness	1.61	
Temporary Hardness . .	—	
Permanent Hardness . .	—	
Chlorine (Chlorides) . .	Absent	
Iron, Lead, Copper, Zinc .	Absent	

Reaction	Neutral to litmus.
Colour	Good.
Clarity or Turbidity . .	Quite clear.
Odour	None.

Remarks.—The chemical analysis of this sample indicates a water of good quality.

Notes.—Comparison of the above with the previous report is instructive.

SEWAGE, TRADE WASTE, AND EFFLUENTS

SEWAGE, trade waste, and effluents are analysed for the purpose of deciding whether their impurity is excessive, and likely to cause a nuisance if discharged into rivers or streams. The whole question has had the benefit of critical inquiry by the Royal Commission on Treating and Disposing of Sewage, which issued a final report in 1915. Present-day standards and methods of analysis are founded on the authoritative reports of this Commission.

COLLECTION OF SAMPLES

The most suitable vessels for collecting samples are clear-glass, stoppered bottles of about 1 litre capacity, which have been previously cleaned in the same manner as for water samples. They should be completely filled. In order to standardise, to some extent, the time between the taking of the sample and its examination, the latter should be commenced forty-eight hours after collection. If delayed beyond this time, the sample should be kept in a cold dark place.

The most reliable tests are the estimations of dissolved oxygen absorption, and suspended solids.

ABSORPTION OF DISSOLVED OXYGEN IN FIVE DAYS AT 18.3° C.

The principle of the determination is that the sample is diluted with well-aerated water of good quality, and an estimation is made of the dissolved oxygen absorbed from the water by the sample.

Rideal and Stewart's modification of Winkler's method.¹

Reagents required:

Sulphuric Acid.—90 cc. of concentrated sulphuric acid with 10 cc. of water.

Potassium Permanganate.—1 gm. KMnO_4 is dissolved in water and made to 250 cc.

Potassium Oxalate.—2 gm. of the crystallised salt in 100 cc.

Manganous Chloride.—33 gm. of the crystallised salt in 100 cc.

Potassium Hydroxide and Potassium Iodide.—70 gm. of potassium hydroxide and 10 gm. of potassium iodide are dissolved together and made to 100 cc.

Hydrochloric Acid.—Concentrated, free from chlorine.

Standard Sodium Thiosulphate.—6.205 gm. of crystallised sodium thiosulphate is dissolved in water and made to 500 cc. 1 cc. = 0.4 mgm. oxygen.

Starch Solution, as indicator.

Process:

The sample is well mixed and 25 to 100 cc. of sewage, or 500 cc. if effluent, is measured in a graduated flask and placed aside for the suspended solids determination (page 120).

A litre of good tap water is brought to 18° C. and shaken in a large flask; a few seconds are allowed for the air bubbles to escape. The sample is also brought to the same temperature, and shaken in the bottle for about half a minute. 25 cc. of sewage (10 cc. if very strong), or 250 cc. of effluent, is added to the water in the flask, and gently but thoroughly mixed. Two clean well-stoppered bottles of known capacity, 450 to 480 cc., are quietly and completely filled with the mixture; the bottles are left unstoppered for five minutes to allow air bubbles to escape. The stoppers are now inserted. In one bottle the dissolved oxygen is estimated immediately, as described below; the other is placed in an incubator at 18.3° C. for five days, at the end of which time it is similarly tested. The difference in the amount present gives the quantity absorbed.

¹ *Analyst*, vol. xxvi., and appendix of Eighth Report of Royal Commission on Treating and Disposing of Sewage, 1913.

To the diluted sample in the bottle, 1 cc. of sulphuric acid, and sufficient potassium permanganate, about 0.5 cc. at a time, to leave a slight trace after mixing and standing stoppered for twenty minutes, is added. Potassium oxalate is then added drop by drop to destroy the excess of permanganate, as shown by the complete disappearance of the pink colour. 1 cc. of manganous chloride is now added from a pipette, dipping as far down in the liquid as possible, and then 4 cc. of the solution of potassium hydroxide and potassium iodide. The stopper is replaced and the contents are thoroughly mixed by inverting several times, the bottle being held by the neck. When the precipitate has settled, 5 cc. of hydrochloric acid is added from a pipette, the bottle is re-stoppered, and the contents are mixed as before; the bottle is now allowed to stand for ten minutes protected from light. 20 cc. of the liquid is removed with a pipette, and the remainder is titrated with standard sodium thiosulphate, using starch solution as indicator. The dissolved oxygen is then calculated to parts per 100,000.

EXAMPLE :

250 cc. of effluent added to 1 litre of tap water, dilution = 1 in 5.

Before incubation.

Capacity of bottle, 476 cc.

Standard sodium thiosulphate required = 10.55 cc.

As 20 cc. of the liquid is removed prior to titration, 456 cc. of diluted sample require 10.55 cc. sodium thiosulphate; the small quantities of sulphuric acid, potassium permanganate, and potassium oxalate used need not be taken into consideration.

1 cc. sodium thiosulphate solution = 0.4 mgm. oxygen; \therefore 10.55 cc. = 4.22 mgm. oxygen in 456 cc. = 0.9254 mgm. in 100 cc.

\therefore Dissolved oxygen present = 0.9254 parts per 100,000.

After incubation.

Capacity of bottle, 467 cc.

Standard sodium thiosulphate required = 2.60 cc.

447 cc. of diluted sample requires 2.60 cc. sodium thiosulphate solution.

1 cc. sodium thiosulphate solution = 0.4 mgm. oxygen, 2.60 cc. = 1.04 mgm.

1.04 mgm. oxygen in 447 cc. = 0.2327 mgm. in 100 cc.

\therefore Dissolved oxygen present = 0.2327 parts per 100,000.

Dissolved oxygen absorbed by the diluted sample in five days at 18.3° C.
= 0.9254 - 0.2327 = 0.6927 parts per 100,000.

Sample was diluted to 1 in 5, \therefore the dissolved oxygen absorbed by sample
= 0.6927 \times 5 = 3.46 parts per 100,000.

SUSPENDED SOLIDS

A Gooch crucible is prepared with a layer of asbestos floss about 0.2 cm. deep, well washed, dried, and weighed until constant. 25 to 500 cc. of the sample, according to the quantity of suspended solids present, is filtered through the crucible fixed in a pressure filter flask. The measured quantity should be allowed to settle before filtration so that the major portion of the suspended matter does not enter the crucible until most of the liquid has been filtered. The asbestos is moistened with the sample, and only very gentle suction is applied at first; no portion of the sample is passed through the filter more than once. The residue is washed, and dried in an air oven at 105° C. until constant in weight.

Below are given two analyses: (1) sewage, (2) the effluent after treatment of this sewage.

	Parts per 100,000.	
	(1) Sewage.	(2) Effluent.
Suspended solids	1357.20	2.18
Dissolved oxygen absorbed in five days	29.71	1.96

STANDARDS RECOMMENDED BY THE ROYAL COMMISSION ON TREATING AND DISPOSING OF SEWAGE

Sewage Matter ¹

‘(a) The law should be altered so that a person discharging sewage matter into a stream shall not be deemed to have committed an offence under the Rivers Pollution Prevention Act, 1876, if the sewage matter is discharged in a form which satisfies the requirements of the prescribed standard.’

‘(b) The standard should either be the general standard or a special standard which will be higher or lower than the general standard as local circumstances require or permit.’

‘(c) An effluent in order to comply with the general standard must not contain as discharged more than 3 parts per 100,000 of suspended matter, and with its suspended matters included must not take up at 65° F. (18.3° C.) more than 2.0 parts per 100,000 of dissolved oxygen in five days. This general standard should be prescribed either by Statute

¹ Eighth Report, 1912.

or by Order of the Central Authority, and should be subject to modifications by that Authority after an interval of not less than ten years.'

'(d) In fixing any special standard, the dilution afforded by the stream is the chief factor to be considered. If the dilution is very low it may be necessary for the Central Authority, either on their own initiative or on application by the Rivers Board, to prescribe a specially stringent standard, which should also remain in force for a period of not less than ten years.'

'(e) If the dilution is very great the standard may, with the approval of the Central Authority, be relaxed or suspended altogether. Our experience leads us to think that, as a general rule, if the dilution, while not falling below 150 volumes, does not exceed 300, the dissolved oxygen absorption test may be omitted and the standard for suspended solids fixed at 6 parts per 100,000. To comply with this test no treatment beyond chemical precipitation would ordinarily be needed. If the dilution, while not falling below 300 volumes, does not exceed 500, the standard for suspended solids may be further relaxed to 15 parts per 100,000. For this purpose tank treatment without chemicals would generally suffice if the tanks were properly worked and regularly cleansed. These relaxed standards should be subject to revision at periods to be fixed by the Central Authority, and the periods should be shorter than those prescribed for the general or for the more stringent standards.'

'(f) With a dilution of over 500 volumes all tests might be dispensed with, and crude sewage discharged subject to such conditions as to the provision of screens or detritus tanks as might appear necessary to the Central Authority.'

Trade Wastes which cannot be taken into Sewers ¹

Coal Washing.—The effluent should not contain more than 4 parts of suspended solids per 100,000. In a number of cases this standard might be relaxed.

Tin, Lead, and Zinc Mines, China Clay Works, Stone Quarries, and Stone Polishing Works.—Provisionally a standard of 6 parts of suspended solids per 100,000. In certain cases the standard might be relaxed or wholly dispensed with.

¹ Ninth Report, 1915.

Tin-plating, Galvanising, and Wire Drawing.—The stronger liquids must not in any circumstances be allowed to discharge into streams. The wash waters should be neutralised and settled. The standard for the wash waters should be 6 parts of suspended solids per 100,000.

Paper Mills where Wood Pulp alone is used.—The effluent should not contain more than 4 parts of suspended solids per 100,000.

Paper Works (Esparto and Rag Paper—Esparto and Wood Pulp Paper, Brown Paper, and Wall Paper).—The effluent should not contain more than 6 parts of suspended solids per 100,000.

Breweries and Maltings.—The effluents should not contain more than 4 parts of suspended solids per 100,000, and should not take up more than 4 parts of dissolved oxygen per 100,000 in five days.

Distilleries.—A standard of 3 parts suspended solids and 2 parts dissolved oxygen absorption in five days is recommended.

Shale Oil Distillation.—The standards are 4 parts of suspended solids per 100,000, and 4 parts dissolved oxygen absorption per 100,000 in five days.

Wool Scouring Liquor.—The suspended solids must not exceed 6 parts per 100,000.

Woollen Dyeing, Piece and Yarn Scouring and Blanket Scouring Liquors (occurring either separately or in any combination). Wool Scouring, with Piece and Yarn Scouring and Dye Liquors.—The standard is 4 parts of suspended solids per 100,000.

Cotton Dyeing and Cotton Printing.—The cotton-dye liquor should not contain more than 4 parts of suspended solids per 100,000, and the liquor from the print works not more than 6 parts.

Bleaching.—It is recommended that the suspended solids should not exceed 6 parts per 100,000.

Tannery Waste, Leather Dressers' Waste, and Fellmongers' Waste.—The standard suggested is 4 parts of suspended solids and 4 parts dissolved oxygen absorption in five days per 100,000.

Dairy Waste.—The standard is the same as in the previous case.

MILK AND CREAM

MILK

IN this country the milk supply is derived almost exclusively from the cow, and it is to be understood that except where specific mention is made to the contrary, it is fresh milk from this source that is discussed in the following pages. Milk from other animals is examined by the same methods.

The undernoted analysis gives the average percentage composition of milk :

Fat	.	.	3.7	
Non-fatty solids	9.0	{	Albumen	0.45
		{	Lactose	4.72
		{	Casein	3.09
		{	Ash	0.74
Water	.	.	87.3	

The natural causes of variation in quality are many. Some breeds of cows yield much richer milk than others, and the milk of individuals of the same breed also varies, although the average composition of that from a herd is comparatively constant. Unfamiliar conditions, causing the animal to be nervous, have a detrimental effect on the quality of the milk, and milking at irregular intervals causes variations in the fat content. The period of lactation is another determining factor.

The quality of the milk obtained at one milking differs widely according to the stage of the process reached. The first milk, 'fore milk,' is generally exceedingly poor, while the last, the 'strippings,' is very rich. It is evident that, to take an average sample from one cow, it is essential that the milking be complete.

In drawing samples of milk the bulk quantity is previously thoroughly mixed by pouring it several times into, and back

from, a dry vessel of sufficient size to contain the whole. Simple stirring, particularly if the milk has stood for some time, is frequently ineffective. In taking the samples a clean dry bottle of about 200 cc. capacity is filled.

The chief forms of sophistication consist in the addition of water or of separated or skimmed milk, the removal of fat, and the addition of preservatives.

By the Sale of Milk Regulations, 1901, made by the Board of Agriculture, it is enacted that, for the purposes of the Sale of Foods and Drugs Act, 1875-1899, it shall be presumed until the contrary is proved :

(1) Where a sample of milk (not being sold as skimmed or separated or condensed milk) contains less than 3 per cent. of milk fat, that the milk is not genuine by reason of the abstraction therefrom of milk fat or the addition thereto of water.

(2) Where a sample of milk (not being sold as skimmed or separated or condensed milk), contains less than 8.5 per cent. of milk solids other than milk fat, that the milk is not genuine by reason of the abstraction therefrom of milk solids other than milk fat, or by the addition thereto of water.

And by the Sale of Milk Regulations, 1912, that :

(3) Where a sample of skimmed or separated milk (not being sold as condensed milk) contains less than 8.7 per cent. of milk solids, that the milk is not genuine by reason of the abstraction therefrom of milk solids other than milk fat or the addition thereto of water.

By the Public Health (Milk and Cream) Regulations, 1912, made by the Local Government Board :

(4) The addition of preservatives to milk is prohibited.

(The expression 'milk' here includes separated, skimmed, condensed, and dried milk; for the purpose of these regulations neither cane nor beet sugar is to be regarded as a preservative).

In the analysis of milk it is usually only necessary to determine the specific gravity, the total solids, the fat, non-fatty solids by difference, and the ash, and to test for preservatives.

The sample should be thoroughly mixed immediately previous to commencing each determination.

SPECIFIC GRAVITY

Milk direct from the cow contains a considerable quantity of air, and if tested at once will give a fallacious specific gravity reading. The test can be made after the elapse of about an hour and a half.

Westphal Balance

The instrument is assembled as shown in Fig. 19. The beam is brought to swing equally about the point by moving

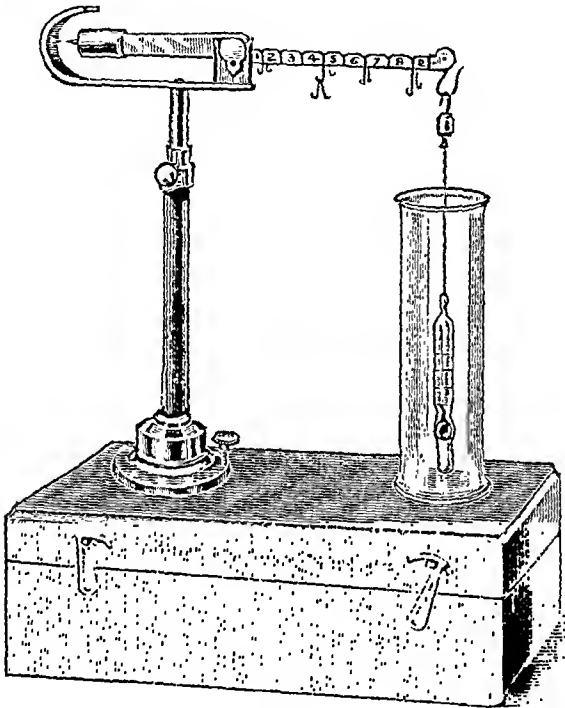
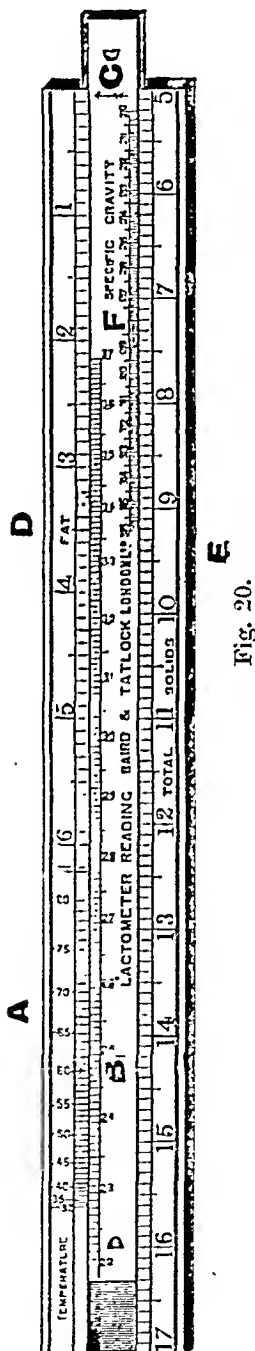


Fig. 19.

the screw weight, and slight alterations in adjustment can be made by the levelling screw-leg. The glass jar is then nearly filled with the milk, and the plummet is immersed in the liquid; the upthrust, equal to the weight of displaced liquid, puts the balance out of equilibrium. Riders are placed on the beam until equilibrium is restored. These riders are four in number. The largest, placed on the extreme end of the beam (the hook from which the plummet is suspended), denotes a specific gravity of 1000 (water=1000), on the division marked 9 it denotes 900, on division 8, 800, and so on. In the same way

the second largest rider indicates 100, 90, 80, etc., the third largest rider reads 10, 9, 8, etc., and finally the smallest rider shows 1.0, 0.9, 0.8, etc., according to the division of the beam on which it is placed.



EXAMPLE :

The largest rider is at the extreme end of the beam, the next largest at division 3, the third largest at division 4, and the smallest at division 7. Then the specific gravity is $1000 + 30 + 4 + 0.7 = 1034.7$.

The specific gravity varies with the temperature, and, if necessary, a correction to 15.5° C. (60° F.) is made. As soon as the reading has been obtained a Fahrenheit thermometer is placed in the jar, and the temperature recorded about a minute later. The correction can be conveniently made by use of Richmond's Milk Scale (Fig. 20). The specific gravity reading on scale B ('lactometer reading') is placed coincident with 60 on scale A, and opposite the temperature at which the specific gravity was taken is the corrected specific gravity.

EXAMPLE :

Specific gravity is 1033.2 at 53° F.; corrected specific gravity then is 1032.4.

Each figure over 1000 is called a lactometer degree.

A rapid, though not so accurate a test can be made with a lactometer. The milk is placed in a jar at least half an inch greater in diameter than the large bulb of the lactometer. The instrument is then gently dropped in, and in a few seconds, when it comes to rest, the reading can be taken. The eye must be on a level

with the milk surface, and the point noted where the lactometer stem is cut ; capillary attraction causes a film of milk to appear above the actual point of contact.

As in the previous method, a correction is made for temperature if necessary. Lactometers can be obtained containing a thermometer enclosed in the instrument, and the temperature reading is noted on a second scale.

In particular circumstances a very accurate determination of the specific gravity may be required, and this can be made by using a specific gravity bottle.

The bottle (50 cc. is a convenient capacity) is dried in a steam oven, allowed to cool in a desiccator, the stopper inserted, and the whole weighed. The stopper is withdrawn and distilled water added to overflowing. The bottle is then placed in a water bath at 15.5° C. and of sufficient depth to reach the neck. After about half an hour the stopper is gently replaced, the excess water finding an exit through the channel. The external water is removed as rapidly as possible by wiping with a clean dry cloth, and the whole is immediately weighed. This process is repeated until a constant weight is recorded. After rinsing the bottle with the sample the process is repeated, using the milk. From the resulting data the specific gravity is calculated.

EXAMPLE :

Weight of bottle and water	77.5106 gm.
Weight of bottle	27.2941 „
Weight of water	<u>50.2165 gm.</u>
Weight of bottle and milk	79.1376 gm.
Weight of bottle	27.2941 „
Weight of milk	<u>51.8435 gm.</u>

$$\text{Specific gravity at } 60^{\circ} \text{ F.} = \frac{\text{weight of milk}}{\text{weight of water}} = \frac{51.8435}{50.2165} \\ = 1032.4 \text{ (water=1000).}$$

The specific gravity averages 1032, and the normal variation is 1029 to 1034. The reading, unless very abnormal, has little value in itself, but it is of the utmost importance if reviewed in the light of the solids and fat determinations. Water having a lower specific gravity, its addition to milk causes

a reduction in specific gravity; in a more marked degree the removal of fat (lower specific gravity) results in an increase. It is evident, therefore, that by adjusting the quantities it is possible to add water and to remove fat without causing the final product of the sophistication to show any difference in specific gravity.

CREAM

A cream tube is used for estimating cream in milk (Fig. 21). It consists of a glass cylinder graduated downwards to show volumes to 20 or 30 per cent. of the volume to the zero mark. The tube is filled with the sample to the zero mark, and allowed to stand for eight hours, at the end of which time the cream that has risen is read directly in volumetric percentage. A plug of cotton wool is placed in the neck to exclude dust, and it is advisable to add a drop of formalin to prevent curdling.

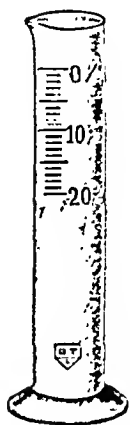


Fig. 21.

The average yield of cream from fresh untreated milk is about 10 per cent. Milk which has been heated will give a very markedly diminished quantity, and may indeed yield practically none. The homogenising of milk prevents separation of the cream more or less completely.

TOTAL SOLIDS

A platinum basin about $2\frac{1}{2}$ inches in diameter, together with a piece of stout platinum wire about $3\frac{1}{4}$ inches long, is weighed after heating and cooling. 10 cc. of the sample is pipetted into the basin and rapidly weighed; if the specific gravity has been determined, it is possible to have a close approximation of the weight ready on the balance. The basin is placed on a steam bath and evaporated to apparent dryness. A skin forms on the surface of the milk which interferes greatly with the evaporation, and it must be gently drawn to one side with the platinum wire; the drying is completed in a steam oven. After cooling in a desiccator, the basin with the residue is weighed as quickly as possible; reheating and weighing is

continued until the loss in weight does not exceed 1 mgm. in half an hour.

EXAMPLE :

Weight of basin + wire + milk	41.6106 gm.
Weight of basin + wire	31.2964 „
Weight of milk taken	<u>10.3142 gm.</u>
Weight of basin + wire + total solids	32.5285 gm. (final)
Weight of basin + wire	31.2964 „
Weight of total solids	<u>1.2321 gm.</u>

There is 1.2321 gm. of total solids in 10.3142 gm. of the sample.

In 100 gm. therefore there is $1.2321 \times \frac{100}{10.3142} = 11.946$ gm.

Total solids = 11.95 per cent.

Some analysts simply pipette the milk into the basin and calculate the weight used from the corrected specific gravity; i.e. suppose this is 1032.4, and 10 cc. is used for the test, then the weight of the milk is taken as 10.324 gm. This modification, except in the hands of those with considerable experience, is liable to introduce considerable error. To prevent the formation of a skin, a few drops of acetic acid and absolute alcohol are sometimes added previous to evaporation, but marked error may be caused by this.

If the corrected specific gravity and fat have been determined, the total solids can be calculated from Richmond's formula :

$$T = 0.25G + 1.2F + 0.14.$$

Where T = Percentage of total solids.

„ G = Lactometer degrees.

„ F = Percentage of fat.

EXAMPLE :

Specific gravity is 1032.4, and the fat, 3.02 per cent.

Then $T = 0.25G + 1.2F + 0.14$

$$= (0.25 \times 32.4) + (1.2 \times 3.02) + 0.14$$

$$= 8.1 + 3.624 + 0.14$$

$$= 11.864$$

Total solids = 11.86 per cent.

The formula is incorporated in the Richmond Milk Scale already referred to. The arrow, C (Fig. 20), is placed coincident with the percentage of fat at D, and opposite the corrected

specific gravity reading on F the percentage of total solids is found on E.

Deficiency of total solids indicates watering or skimming.

ASH

The total solids residue is ignited at a low temperature over an argand flame and weighed until constant. The result is calculated to percentage as before.

EXAMPLE :

Weight of milk taken was that used for estimation of total solids, 10.3142 gm.

Weight of basin + wire + ash 31.3688 gm. (final).

Weight of basin + wire 31.2964 „

Weight of ash 0.0724 „

There is 0.0724 gm. of ash in 10.3142 gm. of milk, therefore in 100 gm.

$$\text{there is } 0.0724 \times \frac{100}{10.3142} = 0.702 \text{ gm.}$$

$$\text{Ash} = 0.70 \text{ per cent.}$$

Ignition at a high temperature causes partial volatilisation of the ash and consequent loss. A high result indicates addition of extraneous matter. A very low result suggests watering.

FAT

Many methods have been evolved for this determination, and each of the methods described has its own particular sphere of usefulness.

Werner-Schmidt Method

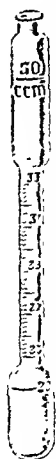


Fig. 22.

10 cc. of the sample is rapidly weighed in a small porcelain basin. The milk is carefully poured into a Stokes' tube (Fig. 22), and the basin washed out with small quantities of concentrated hydrochloric acid until the total volume of liquid in the tube is about 20 cc. The contents are thoroughly mixed by gentle shaking, and the tube is then placed in a boiling-water bath until a dark-brown colour is assumed. This treatment destroys the emulsion of the milk; the fat is set free, and can be extracted with suitable solvents. A short time after removal from the water bath, the tube is placed in cold water until quite

cold. Ether is added to the 50 cc. mark and a good cork is fitted. The tube is slowly inverted and then restored to its original upright position. To prevent warming it is advisable to hold the tube at the ends by pressure of the palms of the hands; rapid movement will cause the formation of a considerable 'fluffy layer,' and prevent complete removal of the fat in ethereal solution. The double inversion is repeated about twenty-five times. The tube is then rapidly rotated for a few seconds in a vertical position between the palms of the hands, and allowed to stand for 10 to 15 minutes to enable the contents to settle. Previously a 200 cc. Erlenmeyer flask has been dried in a steam oven and weighed. With a pipette of convenient size, the clear ether solution which separates above the other liquid, is transferred as completely as possible to the weighed flask. Pending the completion of the extraction, the flask should be corked and set aside in a cool place. Ether is again added to the Stokes' tube, and the operations repeated three times, with 15, 10, and 5 double inversions respectively; the ether solution is in each case transferred to the weighed flask. The flask is connected to a condenser, and the ether distilled off over a steam bath and recovered. It is convenient to employ the Soxhlet apparatus, described in the Adams' method, for the removal of the ether. The flask is dried in a steam oven for two hours and weighed after cooling in a desiccator; the drying is continued until no further loss of weight is recorded. In time, an increase may occur owing to oxidation of the fat.

EXAMPLE :

Weight of basin and milk	40.3774 gm.
Weight of basin	30.0264 „
Weight of milk taken	<u>10.3510 „</u>
Weight of flask and fat	28.0017 „
Weight of flask	<u>27.6232 „</u>
Weight of fat	<u><u>0.3785 „</u></u>

There is 0.3785 gm. of fat in 10.3510 gm. of milk; in 100 gm. there

$$\text{is } 0.3785 \times \frac{100}{10.3510} = 3.657 \text{ gm.}$$

Fat = 3.66 per cent.

A modification of the process is to give only one extraction, with about forty double inversions, after adding ether exactly to the 50 cc. mark. The total volume of ether solution is read, and the fat in 20 cc. is weighed after removing ether and drying. The weight of the fat in the total ethereal solution is calculated. In this modification three-quarters of the 'fluffy layer,' which invariably forms in greater or less degree, is taken as being ether; only approximate results can be obtained.

EXAMPLE :

Clear ether solution = $50 - 24.4 = 25.6$ cc.

'Fluffy layer' = 0.6 cc.; $\frac{3}{4} = 0.45$ cc.

Total ethereal solution = 26.05 cc.

Fat in 20 cc. ethereal solution = 0.2856 gm.; in 26.05 cc. = $0.2856 \times \frac{26.05}{20} = 0.3720$.

From the weight of the milk taken, this is calculated to percentage as already described.

The Werner-Schmidt method gives accurate results, and is more rapid than the Adams' method; it is best for general analysis. The presence of cane sugar causes erroneous results to be obtained, owing to the formation of a substance soluble in ether.

Adams' Method

One end of a strip of absorbent, hard, fat-free paper, 56×6.6 cm., is fastened with a drawing-pin to the edge of the bench. Special paper can be obtained for this process, but it is advisable to do a blank test with one of each box to ensure absolute freedom from ether soluble constituents. 10 cc. of the sample is placed in a porcelain basin and the whole weighed. Holding the free end of the paper in one hand, the milk is carefully poured on and distributed over it; the basin and the residue of milk is weighed, and the difference in weight is the quantity of milk which has been transferred to the absorbing medium. One end of the strip is then held in each hand (the ends should be free from milk), and it is passed rapidly across a 'rose burner' until perfectly dry. The fat is now extracted from the paper in a Soxhlet apparatus (Fig. 23); ACD is the extractor, B a double surface condenser, and E a flask weighed after being dried in a steam oven. The apparatus is assembled as shown in the figure, and with tubes attached to the con-

denser for the entry and exit of water ; the flask rests on a steam bath. The paper is rolled up loosely and placed in C. This part, C, of the extractor is in direct communication with the condenser, but the only channels of communication with the flask are through A and D. Anhydrous ether (page 146) is poured through the funnel of the condenser into C, and when sufficient has been added to reach the level of the top of tube D, it syphons into the flask ; about 30 cc. more ether is added, and the steam bath set in operation. The vaporised ether ascends the tube A, is condensed in B, drops into C, and collects there, dissolving the fat meanwhile ; when the level reaches the top of tube D, syphonage into the flask occurs once more. The process is continuous, and in each cycle, fat which may be present in the coil is transferred to the flask, where it remains. About twenty-five extractions should be given at such a speed as to occupy about three hours in all. The apparatus is useful for the extraction of fat from a large variety of substances. Special fat-free extraction thimbles are used as containers for powders and other solids. When the extraction is complete, the condensed ether is allowed to collect in C, and, just before syphonic action can take place, the burner is extinguished and the ether is run out, through F, into a stock bottle. The contained heat of the water bath is sufficient to cause the remainder of the ether to distil from the flask and collect in C, from which it is removed as before. The recovered ether may be used for other extractions, but it is advisable to redistil before doing so. The process is completed in exactly the same manner as in the Werner-Schmidt

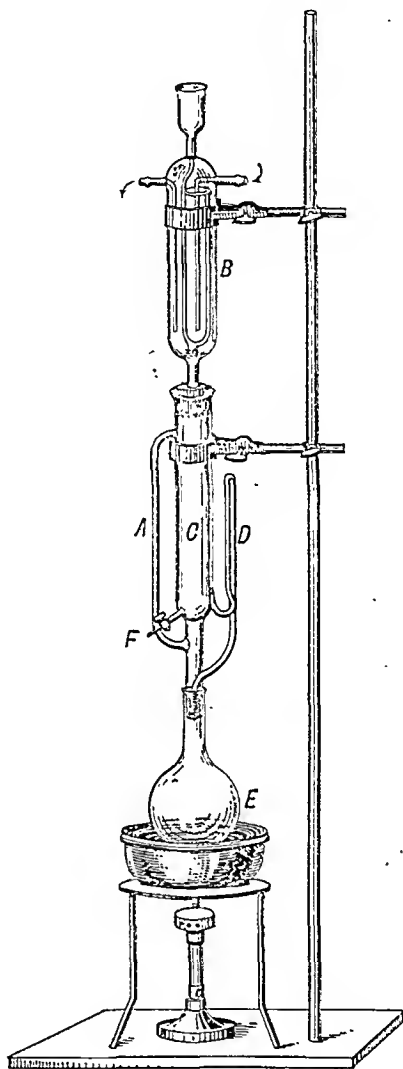


Fig. 23.

method. The flask is disconnected, placed in a steam oven, and dried until constant in weight.

Adams' method, though rather lengthy, is the most accurate, and is of value in legal cases.

By Calculation

The fat can be found by calculation, using the Richmond formula referred to in the total solids determination.

$$\text{If } T = 0.25G + 1.2F + 0.14,$$

$$\text{then } 1.2F = T - 0.25G - 0.14.$$

$$\text{Therefore } F = \frac{5(T - 0.25G - 0.14)}{6}$$

F = percentage of fat, when T = percentage of total solids, and G = lactometer degrees.

EXAMPLE :

A sample of milk contains 12.60 per cent. of total solids, and has a specific gravity of 1032.0 at 15.5° C.

$$\text{Then } F = \frac{5(12.6 - 8 - 0.14)}{6} = \frac{5(4.46)}{6} = 3.72 \text{ per cent.}$$

In using the formula in the Richmond Milk Scale, the corrected specific gravity reading on F (Fig. 20) is placed coincident with the percentage of total solids on E, and opposite the arrow C the percentage of fat is found. This method is useful for checking results obtained by other processes.

Centrifugal Methods

For the routine examination of large numbers of samples in dairies, hospitals and other institutions, the centrifugal methods are the most convenient; results are obtained very rapidly, and are sufficiently accurate for this class of work. Samples which appear deficient in quality can be further examined by more accurate processes. In these methods (for which particular apparatus is used) the fat is set free by suitable reagents, separated by centrifuging, and read off directly on a scale giving gravimetric percentage.

(a) Gerber Method

Reagents required:

Sulphuric Acid, 90 to 91 per cent. (sp. gr. 1.823).

Amyl Alcohol, pure.

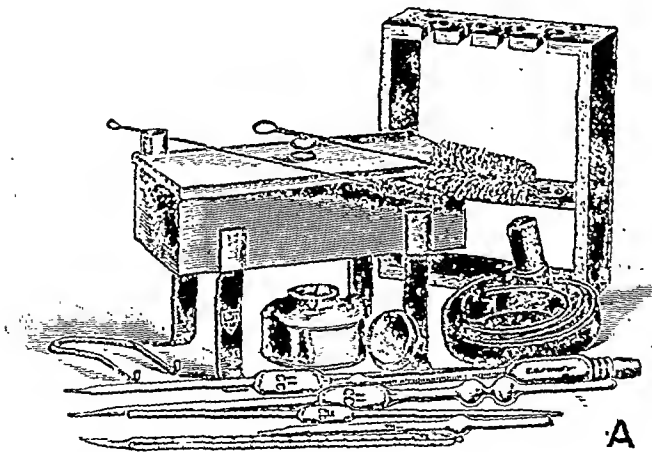
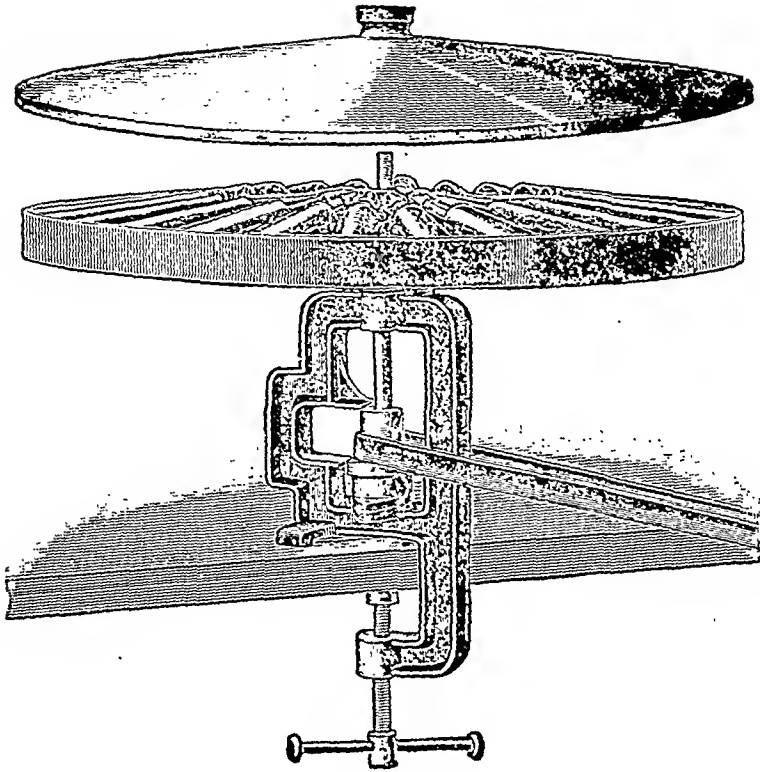


Fig. 24.



Fig. 25.

Process :

Into the milk tube (Figs. 24 A, 25) is pipetted 10 cc. of sulphuric acid, 11 cc. of the sample, and finally 1 cc. of amyl alcohol ; the stopper is inserted tightly and the whole shaken until the coagulated solids are dissolved. It is convenient to examine several samples at the same time. The tube (or tubes) is placed in a clip of the centrifuge (with the corked end pointing to the outside), and rotated at high speed for about four minutes. If only one test is being made, the tube should be balanced in the machine with another full tube ; in the Leffmann-Beam process this is essential. The apparatus having been allowed to come gently to rest, the tube is transferred to a water bath at 60° to 70° C., and after remaining there for one minute the clear fat which has separated is read.

EXAMPLE :

Bottom of fat layer	6.5
Top	„	„	2.8
Fat = 6.5 - 2.8 = 3.7 per cent.							

(b) Leffmann-Beam Method*Reagents required :*

Amyl Alcohol and Hydrochloric Acid Mixture.—25 cc. of pure amyl alcohol is mixed with an equal volume of concentrated hydrochloric acid, cooled, and preserved in a well-stoppered bottle.

Sulphuric Acid.—1. Strong, 96 per cent. (sp. gr. 1.839).
2. Dilute, one part of concentrated sulphuric acid mixed with two volumes of water.

Process :

Into the graduated bottle (Figs. 26 A, 27) is pipetted 15 cc. of the sample, 3 cc. of the amyl alcohol and hydrochloric acid mixture, and, finally, 9 cc. of the strong sulphuric acid. The necks of the bottles are very narrow, and unless care is taken the liquids may overflow. The pipettes should be held just touching the inside edge and allowed to empty slowly. The mixture becomes hot, and mixing is completed by shaking the tube in a longitudinal rotary movement ; the coagulated solids dissolve. The whole is made to the zero mark by the addition of dilute sulphuric acid and the bottle (or bottles) is then

placed in the machine and rotated for four minutes. The percentage of fat which has separated is read.

NON-FATTY SOLIDS

The non-fatty solids are obtained by subtracting the percentage of fat from that of the total solids.

EXAMPLE :

The total solids are 12.26 and the fat is 3.64 per cent., then the non-fatty solids are $12.26 - 3.64 = 8.62$ per cent.

CALCULATION OF ADDED WATER, AND FAT ABSTRACTED

When milk is found to be deficient in quality it is usual to return the degree of sophistication in terms of 'added water' and/or 'fat abstracted.'

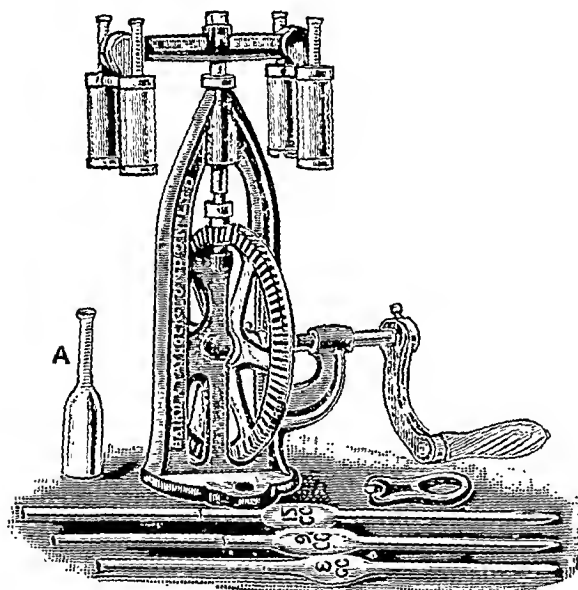


Fig. 26.



Fig. 27.

In calculating 'added water' it is presumed that genuine milk contains a minimum of 8.5 per cent. non-fatty solids. The quantity of genuine milk present is found in terms of the percentage of non-fatty solids of 8.5; this from 100 gives the quantity of added water.

EXAMPLE :

A sample of milk contains 7.42 per cent. of non-fatty solids.

Therefore the percentage of genuine milk present is :

$$\frac{7.42}{8.50} \times 100 = 87.3 \text{ per cent.}$$

Therefore the percentage of added water is $100 - 87.3 = 12.7$ per cent.

In the same way, in calculating the 'fat abstracted,' it is presumed that genuine milk contains a minimum of 3 per cent. of fat, and any deficiency is stated in terms of percentage of 3.

EXAMPLE :

A sample contains 2.66 per cent. of fat.

Therefore the fat abstracted = $3 - 2.66 = 0.34$.

0.34 of 3 in percentage = $\frac{0.34}{3.00} \times 100 = 11.3$ per cent.

Therefore fat abstracted = 11.3 per cent.

DETECTION OF PRESERVATIVES

Until recently preservatives were not infrequently found in milk, but as their addition is now prohibited, and probably also because of the improved methods of partial sterilisation and chilling which are used, their occurrence is comparatively rare.

If the sample becomes sour within twenty-four hours at ordinary room temperature it may be concluded that preservatives are absent.

When present, the preservative is most commonly a boron compound: either boric acid, borax, or a mixture of these.

Boron Compounds

(1) 10 cc. of milk in a porcelain basin is made faintly alkaline with sodium hydroxide, ignited until the majority of the carbon is burnt away, and cooled. The residue is treated with a few drops of dilute hydrochloric acid, a strip of turmeric paper, which has been moistened with oxalic acid solution and dried, is inserted, removed, and dried. If boron compounds are present a pink colour develops which changes to green on treatment with dilute sodium hydroxide.

(1) 10 cc. of milk is ignited as above, and the ash treated with six drops of concentrated sulphuric acid; 2 cc. of absolute alcohol is then added. On lighting the alcohol and stirring vigorously, the presence of boron will be indicated by a green colour in the flame.

Formaldehyde

Formaldehyde in 40 per cent. solution, 'Formalin,' is used

as a preservative. It rapidly disappears from milk, and the tests must be carried out as soon as possible.

(1) *Hehner's Test*.—About 5 cc. of the sample is diluted with the same quantity of water. The liquid is slowly run down the inside of a test tube containing about 3 cc. of concentrated sulphuric acid with one drop of extremely dilute ferric chloride solution. When formalin is present a mauve-coloured ring forms, almost immediately, at the junction of the acid and milk solutions. Pure milk gives a green-coloured ring, rapidly turning brown. The test is extremely sensitive, and only reacts with very small quantities of formalin. If a negative result is obtained further tests should be made with increasing dilutions.

The Hehner test fails to detect formalin when nitrite is present, but Monier-Williams has shown¹ that the test reacts if the milk is subjected to a preliminary treatment. 5 cc. of the sample is treated with 0.5 cc. of a 10 per cent. solution of urea and 1 cc. of 5 per cent. sulphuric acid, and heated in a boiling-water bath for two minutes, cooled, and then examined in the usual way. As at least one preparation of a mixture of formalin and sodium nitrite has been sold, it has been suggested that a test for nitrites (same as for water) should be included in the routine examination of milk.

(2) 10 cc. of milk, 10 cc. of concentrated hydrochloric acid, and one drop of ferric chloride solution are heated together in a porcelain basin with vigorous stirring. The presence of formalin will be indicated by the appearance of a violet colour.

Salicylic Acid and Salicylates, Benzoic Acid and Benzoates

2.5 cc. of a saturated solution of sodium carbonate is added to about 100 cc. of the sample and heated on a steam bath for ten minutes; 5 cc. of 20 per cent. calcium chloride solution is then added. The whole is filtered, cooled, neutralised with dilute hydrochloric acid, mixed with 10 cc. of 10 per cent. copper sulphate solution and then with 5 cc. of 10 per cent. potassium hydroxide. The mixture is filtered and the filtrate, after being acidified with hydrochloric acid, is extracted with about 50 cc. of ether. The ether solution is retained in the

¹ *Local Government Board Food Report*, No. 17, 1912.

separator and gently shaken with about 5 cc. of water. In a few minutes the aqueous portion is run off and the washing is repeated twice. To the washed ethereal solution, 20 cc. of water and two drops of phenolphthalein are added, then dilute sodium hydroxide with thorough shaking, until alkaline. After settling, the alkaline solution is run off and evaporated to about 5 cc. on the steam bath. The cold residue is made very faintly acid with dilute acetic acid, and then a minute drop of fresh 5 per cent. iron alum solution is added. The presence of salicylic acid or salicylates is indicated by a violet coloration ; benzoic acid or benzoates by a buff precipitate.

Fluorine Compounds

50 cc. of the sample is made alkaline with ammonium carbonate and boiled, 5 cc. of 10 per cent. calcium chloride is added, the boiling continued for ten minutes, and the mixture filtered. The precipitate is washed with water, ignited in a platinum basin, and allowed to cool. 1 cc. of concentrated sulphuric acid is incorporated with the residue, and the basin, covered with a small beaker flask half filled with cold water, or watch glass, the base of which is coated externally with stencilled paraffin wax. The whole is placed on the top of a steam oven for one hour. If fluorine compounds are present the bottom of the beaker becomes etched in the places from which the paraffin wax has been removed.

Hydrogen Peroxide

(1) To about 10 cc. of the sample, 5 cc. of fresh unheated milk is added and then two drops of 1 per cent. ortol solution ; the whole is mixed. Hydrogen peroxide is indicated by the appearance of an immediate pink colour.

(2) *Wilkinson and Peter's Test*.—About 0.5 cc. of 2 per cent. benzidine solution and then a few drops of 10 per cent. acetic acid are added to a test tube half full of the sample. The presence of hydrogen peroxide is indicated by the appearance of a blue colour.

Sulphites and Bisulphites

Sulphites and bisulphites may be detected by heating about

50 cc. of the sample with 10 cc. of 10 per cent. phosphoric acid in a narrow-necked flask; if these substances are present sulphur dioxide is evolved and the gas will react to the tests described on page 58.

ARTIFICIAL COLOURING MATTER

The artificial colouring of milk is extensively practised; the quantity of agent required is extremely small, and those employed are, almost without exception, harmless. The colours most commonly used are sulphonated azo dyes, annatto, saffron, and turmeric.

A ready method for detecting these is to note the appearance of the sample when reading the percentage of cream in that determination. The separated milk, in the absence of artificial colouring matter, is paler than the cream; when artificial colouring matter is present the case is reversed.

The presence of sulphonated azo dyes is shown by the appearance of a pink colour on the addition of hydrochloric acid to the fresh sample. (Note in Werner-Schmidt fat determination.)

To detect annatto, saffron, and turmeric, about 50 cc. of the sample is extracted with 20 cc. of ether in a separator; the ethereal extract is evaporated to dryness. The residue is taken up with absolute alcohol, filtered, the filtrate evaporated to dryness, and to the residue, in a porcelain basin, is added one drop of concentrated sulphuric acid. A dark blue coloration turning to green indicates annatto and saffron; the latter finally gives brick-red. The presence of turmeric is denoted by a violet-red coloration.

LACTOSE (MILK SUGAR)

The method for determining lactose is given on page 224; the quantity present is subject to very little variation.

PROTEIN

The total protein in milk, in the rare cases when this estimation is necessary, is obtained by multiplying the total nitrogen determined by Kjeldahl's method (page 174) by 6.38. 5 cc.

of the sample is weighed in a porcelain basin and transferred to the flask; the basin is washed out into the flask with two lots of 10 cc. nitrogen-free sulphuric acid, and the process is continued in the usual manner.

APPARENT DIRT

The volumetric estimation of apparent dirt is conveniently made with Houston's apparatus (Fig. 28). The cylindrical sedimentation apparatus holds 1 litre, and the narrow part immediately above the stopcock is graduated in tenths and hundredths of a cc. After thorough mixing, the sample is poured into the cylinder to the 1000 cc. mark, and 1 cc. of formalin is added and mixed by stirring with a long glass rod. The open end is closed with a plug of cotton wool, and the apparatus is allowed to stand for twenty-four hours, when the 'primary' reading is taken.

EXAMPLE :

Reading = 0.27 cc. = 27 parts
per 100,000.

The small tube shown in the figure is now held under the sedimentation apparatus and the stopcock of the latter is sharply opened and closed several times until all the deposit has been washed into the tube. Distilled water is added to

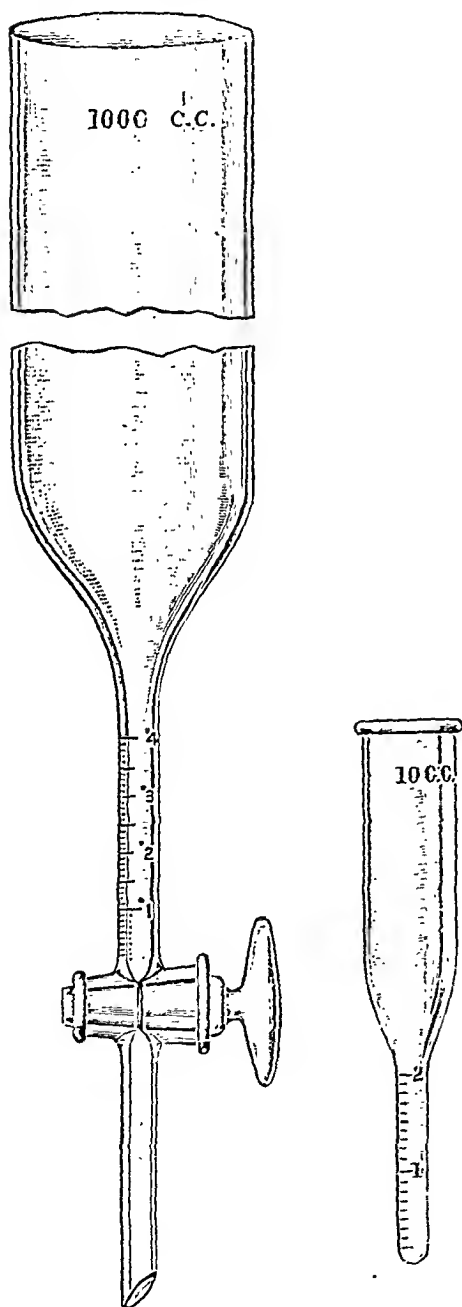


Fig. 28.

about the 10 cc. mark, and the tube is centrifuged for two minutes ; the 'secondary' reading is then made.

EXAMPLE :

Reading, 0.15 cc. = 15 parts per 100,000.

Houston suggests that the quantity of apparent dirt should not exceed ten parts per 100,000 on the primary reading, and five parts on the secondary reading.

ORTOL TEST

This test is sometimes useful for determining whether milk has been boiled or whether boiled milk contains a proportion of unboiled milk. An enzyme present in fresh milk causes the production of a pink colour on addition of the reagents ; heating above 75° C. destroys the enzyme, and this is made evident by the absence of colour. The test may give no evidence of pasteurisation, as in that process a temperature not exceeding 70° C. is commonly employed.

Solutions required :

Ortol Solution, 1 per cent.—This solution is unstable and requires to be prepared fresh each time it is required. It is convenient to dissolve 0.05 gm. in 5 cc. of water.

Hydrogen Peroxide, 10 volumes.

Method :

To about 10 cc. of the sample in a test tube is added one drop of ortol solution, mixed, and then five drops of hydrogen peroxide. The appearance of a pink colour within ten seconds shows that the milk, or a portion of it, has not been heated above 75° C.

INTERPRETATION OF MILK ANALYSIS RESULTS

It will be useful to consider at this stage a few typical milk analyses :

No. 1. Total solids	12.53 per cent.
Fat	3.67 „
Non-fatty solids	8.86 „
Specific gravity	1032.0

Remarks.—A genuine milk of good average quality.

No. 2. Total solids	10.35 per cent.
Fat	3.12 „
Non-fatty solids	7.23 „
Specific gravity	1027.4

Remarks.—The deficiency in non-fatty solids and low specific gravity indicates that the milk is not genuine; calculation from the first-named figure shows it to contain 15 per cent. of added water.

No. 3. Total solids	10.57 per cent.
Fat	2.55 „
Non-fatty solids	8.02 „
Specific gravity	1031.8

Remarks.—The analysis of this sample shows it to be adulterated. As there is a marked deficiency in both fat and non-fatty solids, and the specific gravity does not deviate from the normal, it would appear that fat has been abstracted and water also added. By calculation from the percentage of fat it is found that 15 per cent. has been abstracted, and from the non-fatty solids the addition of 5.7 per cent. of water is indicated.

No. 4. Total solids	12.16 per cent.
Fat	3.32 „
Non-fatty solids	8.84 „
Specific gravity	1032.1
Cream	4.3 „

Remarks.—A genuine sample. The low percentage of cream indicates that the milk has been pasteurised or homogenised.

No. 5. Total solids	13.90 per cent.
Fat	5.13 „
Non-fatty solids	8.77 „
Specific gravity	1030.4

Remarks.—The analysis of this sample indicates a milk of exceptionally good quality.

No. 6. Total solids	10.83 per cent.
Fat	2.16 „
Non-fatty solids	8.67 „
Specific gravity	1033.5

Remarks.—This milk is deficient in fat. By calculation it is found that 28 per cent. has been abstracted.

No. 7. Total solids	17.85 per cent.
Fat	9.22 „
Non-fatty solids	8.63 „
Specific gravity	1027.8

Remarks.—This milk is abnormal. The extraordinary rich quality is due to defective sampling. The sample was taken from the top in a churn which had stood for some time, and the cream had not been properly mixed with the bulk.

ANALYSIS OF MILK WHICH HAS TURNED SOUR

When milk turns sour the non-fatty solids decompose but the fat undergoes little alteration. The proteins are comparatively unaffected, but a greater or less quantity of lactose is converted by fermentation into lactic acid; small quantities of alcohol, butyric acid, acetic acid, aldehyde, carbon dioxide, and ammonia are also produced. It will be evident, therefore, that some of the ordinary processes of analysis are inapplicable.

Specific Gravity

Richmond's Modification of Wiebull's Method

(1) To 100 cc. of the sample, 5 cc. of a solution of ammonia (one part ammonia, sp. gr. 0.880, with four of water) is added and well mixed; the curd dissolves. The specific gravity of the mixture is determined by the Westphal Balance and (2) that of a similar mixture made with fresh milk; (3) the specific gravity of the fresh milk itself is taken. The addition of ammonia causes lowering of the specific gravity, the extent of which is shown by the difference between the determinations (2) and (3). This amount is added to the sample mixture reading (1), and the result is the original specific gravity of the sample.

EXAMPLE :

(1) Sp. gr. of sample and ammonia mixture	1029.5
(2) „ fresh milk and ammonia mixture	1029.7
(3) „ fresh milk itself	1032.4

Then $1032.4 - 1029.7 = 2.7$ and $1029.5 + 2.7 = 1032.2$.

Therefore original specific gravity of sample = 1032.2.

Fat, Non-Fatty Solids, Total Solids

Maceration Method

A flat-bottomed platinum basin is weighed together with a small glass rod with a flattened end. 10 to 12 cc. of the sample is placed in the basin and rapidly weighed. Two drops of phenolphthalein (1 per cent. in absolute alcohol) are added, and the liquid is neutralised with N/10 strontium hydroxide from a burette, as shown by the appearance of just a faint trace of permanent colour; the quantity of strontia required is noted. The whole is evaporated on a steam bath until it attains a friable condition. In the meantime a 7 cm. filter has been dried in a weigh bottle until constant in weight. When the evaporated solids are still warm, 20 cc. of dehydrated ether (distilled over granulated calcium chloride) is added and thoroughly incorporated with the solids by stirring with the glass rod. The solids are allowed to settle, and the ethereal solution of fat is carefully decanted through the weighed filter paper and collected in a weighed flask. The maceration is repeated eight times with about 10 cc. of ether in each case, the solids always being broken up as completely as possible. The filter is well washed with warm ether, and dried in a steam oven until constant in weight; the increase in the weight gives the small quantity of solids on the filter. The solids remaining in the basin are similarly dried and determined. The total weight of the solids, less 0.0045 gm. for each cc. of N/10 strontium hydroxide added, gives the non-fatty solids in the weight of milk taken. The ether, distilled from the solution of fat in the flask, and the residue is dried until constant in weight.

EXAMPLE :

Weight of basin and rod + milk	41.5854 gm.
„ „ basin and rod	29.6234 „
„ „ sample taken	<u>11.9620 gm.</u>

3.65 cc. N/10 strontium hydroxide required for neutralisation.

Non-Fatty Solids.

Weight of weigh bottle and filter + non-fatty solids	18.5229 gm.
„ „ weigh bottle and filter	18.4916 „
„ „ non-fatty solids	<u>0.0313 gm.</u>

Weight of basin and rod + non-fatty solids	30.6452 gm.
„ „ basin and rod	29.6234 „
„ „ non-fatty solids	<u>1.0218 gm.</u>

Total weight of non-fatty solids found = $0.0313 + 1.0218 = 1.0531$ gm.
 From this must be deducted 0.00428 gm. for each cc. of strontium hydroxide used in neutralisation, therefore for 3.65 cc. the correction is $0.00428 \times 3.65 = 0.0156$.

Therefore the weight of non-fatty solids in 11.962 gm. of sample = $1.0531 - 0.0156 = 1.0375$ gm. = 8.67 in 100 gm.

\therefore Non-fatty solids = 8.67 per cent.

Fat.

Weight of flask + fat	39.8139 gm.
„ „ flask	39.4198 „
„ „ fat	<u>0.3941 gm.</u>

0.3941 gm. of fat in 11.962 gm. of sample = 3.29 in 100 gm.

\therefore Fat = 3.29 per cent.

Total Solids.

Total solids = non-fatty solids + fat = $8.67 + 3.29 = 11.96$ per cent.

An analysis of milk which has turned sour, carried out in accordance with the foregoing directions, will yield results sufficiently accurate for all practical purposes. In extremely accurate determinations various small corrections, additive and subtractive, are made, the net result of which averages a slight addition.

SKIMMED AND SEPARATED MILK

When cream is removed from milk by hand the remaining liquid is known as skimmed milk, and when direct mechanical means are employed, as separated milk. The mechanical method results in a much more complete removal of fat; separated milk rarely contains more than 0.3 per cent. of fat, while skimmed milk averages 1.0 per cent.

The analysis is the same as for full cream milk, but the only determination necessary, apart from that for preservatives, is that for total solids, which must not be less than 8.7 per cent.

BUTTERMILK

Buttermilk is examined by the methods given for sour milk.

CONDENSED MILK

There are four varieties of condensed milk in common use :¹

(1) Full cream, fully sweetened, containing 35 to 40 per cent. of sucrose.

(2) Full cream, partially sweetened, containing sucrose not exceeding 18 per cent.

(3) Full cream, unsweetened.

(4) Machine skimmed, fully sweetened, containing 38 to 45 per cent. sucrose.

(The 'sucrose' used is almost invariably beet sugar; in the cheaper brands a proportion of glucose is sometimes added.)

In the manufacture of condensed milk, the milk is pasteurised and concentrated in vacuo, generally to about one-third its original volume. The fully sweetened milks contain about 15 per cent. of added sugar previous to concentration. In the machine skimmed make, the milk fat is first removed by mechanical separation. Preservatives are generally absent, but occasionally boron compounds are found.

The various kinds of condensed milk have the average percentage composition shown in the table subjoined.

AVERAGE PERCENTAGE COMPOSITION OF CONDENSED MILK

	Full cream, fully sweetened.	Full cream, partially sweetened.	Full cream, unsweetened.	Machine skimmed, fully sweetened.
Total Solids .	74.4	45.2	35.2	71.8
Fat .	10.1	11.4	11.1	1.2
Non-fatty Solids .	64.3	33.8	24.1	70.6
Protein .	8.9	8.9	8.9	10.0
Lactose .	14.1	14.1	13.3	14.3
Sucrose .	39.2	8.7	—	44.0
Ash .	2.1	2.1	1.9	2.3
Water .	25.6	54.8	64.8	28.2

¹ Report to Local Government Board by Dr. Coutts. Food Reports, No. 15, 1911.

15 to 20 gm. of the sample is weighed in a small beaker and dissolved in about 50 cc. of warm water. This is poured into a 100 cc. graduated flask, and the beaker is washed out with successive small quantities of water, making, in all, just under 100 cc. The diluted milk is cooled, made to the mark, and used as a stock solution; it is thoroughly mixed each time before transferring portions for the tests below.

Total Solids and Ash

10 cc. of the stock solution is accurately pipetted into a weighed platinum basin, and the total solids and ash are determined as in fresh milk. The amounts found are those in one-tenth of the weight originally taken.

Fat

Fat is estimated by the Adams' process as previously detailed; 10 cc. of the stock solution is placed direct on the absorbent paper. It is advisable to give forty extractions over a period of about five hours.

The fat may also be determined by the Gerber and the Leffmann-Beam centrifugal methods.

The stock solution is treated as ordinary milk; the fat reading is multiplied by 100 and divided by the weight of sample used for dilution, to obtain the percentage present. Unsweetened milk may be tested direct, but sweetened milks require preliminary treatment by Leach's method. To the measured portion of stock solution in the tube 3 cc. of 5 per cent. copper sulphate solution is added to precipitate proteins and fat; the bottle is well shaken and centrifuged at high speed. The supernatant fluid containing the sugar is removed with a pipette made from a piece of tubing drawn out to a fine bore and fitted with a teat at the other end. More water is added to make the former volume, and after shaking, the bottle is again centrifuged; this process is repeated twice, the supernatant fluid being removed each time as before. The process, according to the method employed, is then completed as already directed.

Protein

Protein is determined in 10 cc. of the stock solution as for fresh milk.

Lactose, Sucrose, and Glucose

The sugars are estimated by the methods given on page 224.

Preservatives

The presence of preservatives is uncommon, but boron compounds have been found, and it has been stated that formalin is also used. The examination is similar to that of ordinary milk.

Degree of Condensation

In the case of full cream milks, the degree of condensation is obtained by dividing the percentage of fat found, by 3·7, the average amount in whole milk; and in skimmed milk, by dividing the total solids, less sucrose and glucose, by 9·2, the average amount in skimmed milk.

EXAMPLES :

- (1) Full cream condensed milk contains 10·73 per cent. of fat.

$$\text{Therefore degree of condensation} = \frac{10.73}{3.7} = 2.9.$$

- (2) Skimmed condensed milk contains 74·15 per cent. total solids, and 43·80 per cent. of sucrose.

$$\text{Therefore degree of condensation} = 74.15 - 43.80 = 30.35 \text{ divided by } 9.2 = 3.3.$$

MILK POWDERS AND DRIED MILK

In the manufacture of milk powders and dried milk, the whole milk is generally employed. The milk is evaporated by various methods, and commonly a trace of sodium carbonate is added previously, to neutralise acidity and to increase the solubility of the product. Sometimes sucrose is also added.

The following analysis gives the percentage results of a typical sample :

Moisture	6.4 per cent.
Ash	6.2 „ „
Fat	25.4 „ „
Lactose	33.5 „ „
Sucrose	1.3 „ „
Protein	27.2 „ „

Moisture.—5 gm. is dried in a steam oven until constant in weight.

Ash.—The residue from the moisture determination is treated as in milk.

Fat.—Mohs's Method.¹ The sample is ground fine, and 1.5 gm. is heated with 50 cc. of water, and 6 cc. of hydrochloric acid (five parts of concentrated hydrochloric acid with three of water), for one and a half hours in a boiling water bath. The solution is cooled, made neutral to methyl orange with a strong solution of sodium hydroxide, then made acid with dilute hydrochloric acid and filtered. The filter with its contents is dried at 105° C. for two hours, placed in an extraction thimble, and extracted with ether in a Soxhlet apparatus for six hours.

Lactose and Sucrose.—The sample is examined as described on page 224. Sucrose may be detected as on page 152.

Protein.—2 gm. is used for the determination by Kjeldahl's method (page 174).

CREAM

Cream contains the same constituents as milk ; the essential difference is its much higher fat content. The composition varies greatly, and for this reason it has not been found possible to formulate standards.

The most common adulterations are the inclusion of an excess of milk and the addition of preservatives and thickening agents.

By the Public Health (Milk and Cream)-Regulations, 1912, the addition of thickening substances to any cream, and also

¹ *Zeitsch. ges. Getreidew.*, 1916, viii. 37-41.

the addition of preservatives to cream containing less than 35 per cent. of fat, is prohibited. In cream containing 35 per cent. or more of fat, the only preservatives permitted are boric acid or borax (or mixtures of these), or hydrogen peroxide, and their presence must be declared. In an amending order to these regulations (1917), it is further enacted that when the presence of boron compounds is permissible, they must not exceed 0.4 per cent. calculated as H_3BO_3 . For the purpose of the regulations sucrose is not to be regarded as a thickening substance or preservative.

The analysis is on similar lines to that of milk, with the modifications indicated below. About 1 gm. only is used for the usual determinations.

Fat

Werner-Schmidt Method.—About 1 gm. diluted with 9 cc. of water is treated as in milk.

Detection of Cane or Beet Sugar (Sucrose) ¹

Reagents required :

Diphenylamine solution.—5 per cent. solution in 95 per cent. by volume alcohol. 5 cc. of this is mixed with 15 cc. of glacial acetic acid and 30 cc. of a mixture of equal parts of concentrated hydrochloric acid and water. The reagent should be prepared fresh from the alcoholic solution as required.

Ammoniacal lead acetate solution.—110 gm. of neutral lead acetate and 33 gm. of litharge are boiled for half an hour with 150 cc. of water, and cooled. The clear solution is decanted, and reduced to a specific gravity of 1.15 with cold, recently boiled water. Immediately before use, 20 cc. of this solution is mixed with 10 cc. of ammonia (sp. gr. 0.880, one part with two of water).

Process :

1 gm. of the sample is warmed with 10 cc. of water, and then 10 cc. of ammoniacal lead acetate solution is added. The liquid is well shaken and immediately filtered. To about 4 cc.

¹ Report to the Local Government Board, Food Report No. 24, 1918.

of the filtrate, 8 cc. of diphenylamine solution is added, and the whole heated in a boiling water bath for ten minutes. The presence of sucrose is indicated by a blue colour; 0.05 per cent. gives a faint blue, and 0.1 per cent. a very distinct blue colour.

Preservatives

The qualitative examination is made by the same methods described for milk except that Monier-Williams' method must be employed for the detection of benzoic acid, benzoates, salicylic acid, and salicylates. As 0.4 per cent. of boric acid or borax is permitted, the quantitative examination for these boron compounds is also described.

Detection of Benzoic Acid, Benzoates, Salicylic Acid, Salicylates, and Saccharin, Monier-Williams' Method : ¹

Reagents required :

Phosphoric acid, concentrated.

Sodium bicarbonate, 0.5 per cent. solution.

Hydrochloric acid, concentrated.

Ether, sp. gr. 0.720.

Calcium chloride, dry granulated.

Ammonia, sp. gr. 0.880.

Iron alum, 5 per cent. solution.

Process :

About 100 gm. of the sample, acidified with 1 cc. of phosphoric acid, is heated in a porcelain dish on an asbestos gauze, with constant stirring, until all the water is evaporated; the temperature must not rise above 120° C. The fat, which will contain any of the above preservatives, is separated by filtration through a dry filter paper, allowed to cool to about 65° C., and thoroughly shaken with 50 cc. of sodium bicarbonate solution previously heated to the same temperature. The alkaline extract is separated from the fat, in a separator, and filtered through a wet filter paper. One cc. of concentrated hydrochloric acid is added to the filtrate, the whole is cooled,

¹ Report to the Local Government Board by Dr. J. M. Hamilton on the use of preservatives in Cream, 1909, Food Reports, No. 10, 1909.

and extracted three times in a separator with about 15 to 20 cc. of ether in each case. To the total extract an addition of about 1 gm. of calcium chloride is made, and it is allowed to stand about half an hour, with occasional shaking. The ethereal solution is decanted into a small dry flask, and the ether is removed by distillation.

If saccharin is present the residue has a perceptible sweet taste.

The residue is stirred with 1 cc. of ammonia, evaporated to dryness, taken up with four drops of water, and then a minute drop of iron alum solution on a glass rod is added.

A buff-coloured precipitate indicates the presence of benzoic acid or benzoates; a purple coloration, salicylic acid or salicylates.

Estimation of Boric Acid and Borax : Richmond and Miller's Method ¹

Solutions required :

N/10 sodium hydroxide, 1 cc. = 0.004 gm. NaOH and 0.0062 gm. H_3BO_3 .

N/10 sulphuric acid, 1 cc. = 0.0049 gm. H_2SO_4 .

Phenolphthalein, 0.5 per cent. in absolute alcohol.

Process :

10 to 20 gm. of the cream is washed into a beaker with about an equal quantity of water, and, after the addition of half the bulk of phenolphthalein, N/10 NaOH is run in until a pink colour is produced. The whole is boiled and made just acid with N/10 sulphuric acid while still boiling, and then sufficient N/10 NaOH is added to give a faint pink colour. The quantities of alkali and acid required for the various steps to this point in the determination do not require to be noted. An amount of pure glycerine, approximately one-third of the volume of the liquid, is now added, and the whole titrated (without further heating) with N/10 NaOH; each cc. now required represents 0.0062 gm. of boron as boric acid, and this is calculated to percentage in the usual way, after subtracting any alkali required by the same amount of glycerine in a blank test.

¹ *Dairy Chemistry*, by H. Droop Richmond, 1914, p. 87.

EXAMPLE :

20.146 gm. of the sample requires 7.6 cc. of N/10 NaOH after addition of the glycerine.

1 cc. N/10 NaOH = 0.0062 gm. H_3BO_3 , \therefore 7.6 cc. = 0.04712 gm.

0.04712 gm. H_3BO_3 in 20.146 gm. of cream = 0.23 per cent.

Protein

2 gm. only of the sample is used.

Artificial Thickening Agents

The most common thickening agent used is gelatine ; heated starch has also been employed. These can be detected by the methods given below.

Gelatine. Stokes' Test*Solutions required :*

Acid mercuric nitrate solution.—25 gm. of mercury is dissolved in 50 cc. of concentrated nitric acid and the solution is made to 100 cc. with water.

Picric acid.—Saturated aqueous solution.

Process :

To about 10 cc. of the cream is added 25 cc. of water and 2 cc. of acid mercuric nitrate solution ; the mixture is thoroughly shaken and filtered through a dry filter paper. If much gelatine is present the filtrate will not be clear, but this does not interfere with the test. On the addition of 3 cc. of picric acid solution, a yellow precipitate forms either at once or on standing for a few minutes, according to the amount present.

Starch

The addition of a drop of dilute iodine solution in the cold will cause the appearance of a blue colour if starch is present.

BUTTER AND MARGARINE

IN the preparation of butter, lactic fermentation is promoted in cream, and the sour product is churned. The violent agitation causes the fat globules to unite into a granular mass, which is then washed with cold water, and worked into a homogeneous whole after the addition of a small quantity of salt. Though no definite ruling has been given as to the quantity of salt determining the classification of butter as 'fresh' or 'salt,' it is usually understood that the former contains less than 1.5 per cent. 'Milk blended' butter is legally defined as 'any mixture produced by mixing or blending butter with milk or cream (other than condensed milk or cream).' Butter which has become unfit for human consumption is treated, and is known as 'renovated' or 'process' butter. Little is manufactured in this country, but a considerable business exists in America. The process consists in melting the fat, removing the curd by sedimentation, and blowing air through the liquid to disperse bad odours. It is then emulsified by churning with milk, chilled, and the granular product is 'worked' as in ordinary butter manufacture.

Until comparatively recent years, margarine was manufactured almost exclusively from beef fat. By a refining process of fractional crystallisation, and pressing, the oleomargarine is separated from the stearin. The oleomargarine, either with or without admixture of other animal fats, and vegetable fats and oils, is churned with skimmed milk; the milk is previously pasteurised, then inoculated with *Bacillus lacticus* and allowed to sour until the necessary amount of acidity has formed.

Modern methods of refining, together with the development of the process of hydrogenation of oils, have enabled a great number of vegetable origin to be used, and they are being employed in increasing quantities. Those most commonly used are coconut, palm-kernel, cotton-seed, sesame, and arachis oil.

Hydrogenation consists of treatment with hydrogen in the presence of a catalyst, commonly nickel; by this means, liquid oils are converted into solid fats, and soft fats are hardened. In the better qualities of margarine animal fat predominates. In each case, after churning, the product is chilled, and a small quantity of salt is worked into it. It has been pointed out that margarine prepared chiefly from vegetable fats and oils is not equal to butter in nutritive value, owing to the absence of a necessary substance for healthy metabolism, though margarine prepared from animal fat can fully replace butter in this respect.¹

The average percentage composition of butter and margarine is shown in the following tables :

	Butter.	Margarine.
Fat	84.3	84.9
Curd (casein and lactose)	1.0	0.9
Salt	1.6	1.7
Water	13.1	12.5

It will be seen that the composition of butter and margarine, as indicated above, is for all practical purposes the same; the whole difference lies in the nature of the fat.

The sophistication of butter consists in the admixture of foreign fats and an excessive quantity of water and salt. Both butter and margarine very generally contain artificial colouring matter, and a small quantity of preservative, usually a boron compound; the latter should not exceed 0.5 per cent. By the Butter and Margarine Act, 1907, the limit for water in butter and margarine is fixed at 16 per cent.; 'milk blended' butter, which must be sold under a fancy name not suggestive of butter, may contain 24 per cent. Salt in butter should not exceed 6 per cent. By the Sale of Food and Drugs Act, 1899, margarine must not contain more than 10 per cent. of butter fat.

Butter and margarine samples are conveniently collected in 8 oz. wide-mouthed stoppered bottles, and about 4 to 6 oz. is a suitable quantity to obtain.

¹ Drummond and Halliburton, *Journal of Physiology*, 2, 1917.

The examination of butter and margarine may be considered in two parts: first that of the complete sample, and second, that of the fat of the sample.

WATER, CURD, SALT, AND FAT

Water

About 50 gm. of the sample is melted, at as low a temperature as possible, in a large boiling tube; the tube is corked and well shaken. Immediately, about 5 gm. is rapidly and accurately weighed in a platinum basin previously weighed together with a small glass rod. 2 cc. of absolute alcohol is mixed with the quantity, and the whole is dried on a steam bath for two hours, and then in a steam oven for one hour, with occasional stirring; it is allowed to become cold in a desiccator, and weighed. Further periods of one hour, in the oven, are given until the loss of weight does not exceed 2 mgm. A gain in weight may take place owing to oxidation, in which case the lowest weight is taken as final.

Non-Fatty Solids

In the meantime a 7 cm. filter paper has been dried until constant in weight, and the weight ascertained. The residue from the water determination is melted, and filtered through this. The basin is washed out with successive quantities of anhydrous ether from a small wash bottle, and the washings are passed through the filter until every trace of fat is removed. The filter, with the residue of non-fatty solids, is placed in the basin with the rod, and dried for periods of half an hour in the steam oven until constant in weight.

Salt

The filter is replaced in the funnel, and the basin is washed out with small quantities of warm water, through the filter, to dissolve the salt. The filtrate is cooled and titrated with N/10 silver nitrate, using potassium chromate indicator (as in water analysis). Each cc. of the standard solution = 0.00585 gm. sodium chloride.

Curd

The curd is obtained by difference: non-fatty solids—salt = curd.

Fat

The fat may be obtained by difference: 100—(percentage of water+non-fatty solids), or the ethereal solution from the non-fatty solids determination may be collected in a weighed flask, the ether distilled off, and the fat weighed, after drying in the steam oven.

EXAMPLE :

Weight of basin and rod+sample	40.477 gm.
„ „ basin and rod	35.267 „
„ „ sample taken	<u>5.210 gm.</u>

Water.

Weight of basin and rod+sample, before drying	40.4770 gm.
„ „ basin and rod+sample, after drying	39.6486 „
„ „ water	<u>0.8284 gm.</u>

There is 0.8284 gm. of water in 5.210 gm. of sample.

∴ Water=15.90 per cent.

Non-fatty solids.

Weight of weigh bottle+filter paper	14.0320 gm.
„ „ weigh bottle	13.8859 „
„ „ filter paper	<u>0.1461 gm.</u>
Weight of basin and rod+paper+non-fatty solids	35.5416 gm.
„ „ basin and rod	35.2670 „
„ „ paper+non-fatty solids	0.2746 gm.
„ „ paper	<u>0.1461 „</u>
„ „ non-fatty solids	<u>0.1285 gm.</u>

There is 0.1285 gm. non-fatty solids in 5.210 gm. of sample.

∴ Non-fatty solids=2.47 per cent.

Salt.

Filtrate required, 11.7 cc. N/10AgNO₃

Now 1 cc. N/10AgNO₃=0.00585 gm. NaCl,

∴ 11.7 cc. „ =0.068445 gm. NaCl.

There is 0.068445 gm. NaCl in 5.210 gm. of sample.

∴ Salt=1.31 per cent.

Curd.

Non-fatty solids=2.47 and Salt=1.31 per cent.

∴ Curd =2.47—1.31 =1.16 „

Fat.

Water=15.90 per cent. and non-fatty solids=2.47 per cent.

∴ Fat=100—(15.90+2.47)=100—18.37=81.63 per cent.

Examination of the Fat

The melted sample, in the boiling tube, is allowed to remain in a steam oven until quite liquid. A large plug of cotton wool is then placed in the mouth of the tube and gently forced down with a glass rod. The clear fat rises, while the non-fatty solids and water remain at the bottom of the tube.

REICHERT-WOLLNY-POLENSKE PROCESS

This test shows whether the fat from butter is genuine and, in margarine, amongst other information obtained, the presence of an excess of butter fat is revealed.

The fat is saponified with sodium hydroxide and glycerine, and the soap formed is decomposed with sulphuric acid. All the fatty acids are set free, and on distillation, the distillate contains a constant proportion of the volatile fatty acids. The soluble and insoluble volatile fatty acids are separately titrated with N/10 alkali, and the number of cc. required, calculated for 5 gm. of the fat, gives the Reichert-Wollny and Polenske numbers respectively.

Reagents required:

Pure glycerine.

50 per cent. sodium hydroxide solution. 50 gm. sodium hydroxide dissolved in water and made to 100 cc.

Sulphuric acid. 12.5 cc. concentrated sulphuric acid in water to 500 cc.

N/10 barium hydroxide.

90 per cent. alcohol. 450 cc. absolute alcohol with 50 cc. of water.

Phenolphthalein indicator.

Process:

4.8 to 5.2 gm. of the clear fat is accurately weighed in a 300 cc. flask, 20 gm. of glycerine, and then 2 cc. of 50 per cent. sodium hydroxide is added. The whole is heated over a small flame until saponification is complete, as shown by the mixture becoming quite clear. A few pieces of broken porcelain, and then 100 cc. of boiling water are added. The soap

being completely dissolved, 40 cc. of sulphuric acid is added and the flask *immediately* connected to the distillation apparatus shown in Fig. 29. It is important that the dimensions

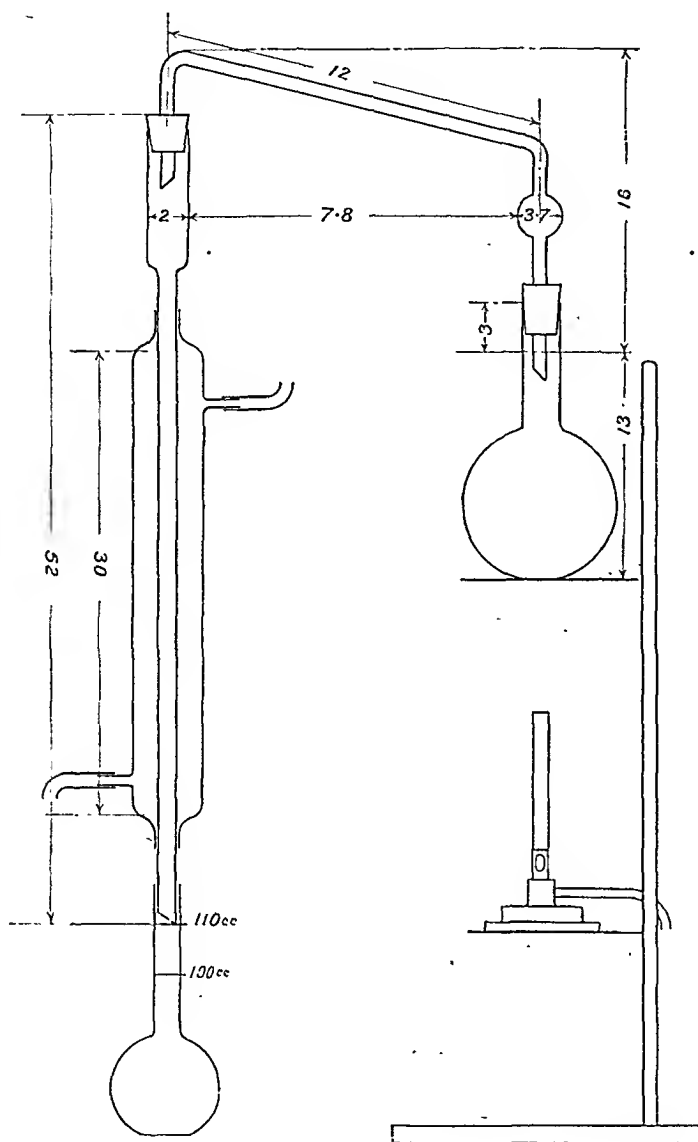


Fig. 29.

of the parts should closely approximate those prescribed. The condenser is 52 cm. long over all, the outer jacket, 30 cm. The splash bulb of the connecting tube has a diameter of 3.7 cm., and the length of the tube between the two bends, a length of

12 cm. From the outside edge of the condenser inner tube, horizontally to the outside edge of the splash bulb tube, is a distance of 7.8 cm. Before commencing the distillation proper, a small flame is maintained under the flask until the insoluble fatty acids have melted; the distillation is continued until 110 cc. of distillate is collected at such a speed as to give this quantity in twenty minutes. The distilling flask is at once removed. Without mixing the distillate in it, the graduated flask is placed for fifteen minutes, in water at about 15° C. reaching externally to above the 110 cc. mark, and is replaced by a 25 cc. measuring cylinder. The condition of the insoluble fatty acids in the distillate should be noted. If more than 10 per cent. of coconut oil is present it forms transparent oily drops. The whole distillate is filtered through a dry 7 cm. filter paper; 100 cc. is collected, and titrated with N/10 barium hydroxide, using phenolphthalein as indicator, and from the result the Reichert-Wollny number is calculated. The remainder of the distillate is discarded. The condenser is washed out with three successive quantities of water (about 18 cc. in all) into the cylinder, which are, in turn, passed through the graduated flask and the filter, and finally rejected. This process is repeated with 90 per cent. alcohol (using about 70 cc.), but the total alcoholic filtrate is collected and titrated with N/10 barium hydroxide as before, and the Polenske number calculated from the result. It is advisable to do blank tests and to make any corrections found necessary.

EXAMPLE :

Weight of fat taken for test 5.134 gm.

Reichert-Wollny number.

100 cc. of distillate requires 28.9 cc. N/10 Ba(OH)₂.

∴ 110 cc. of distillate requires $28.9 \times 1.1 \approx 31.79$ cc. N/10 Ba(OH)₂.

31.79 cc. N/10 Ba(OH)₂ required for 5.134 gm. of fat, ∴ for 5 gm., 30.9 cc. will be required.

∴ Reichert-Wollny (R.W.) number = 30.9.

Polenske number.

Total alcoholic filtrate requires 2.6 cc. N/10 Ba(OH)₂.

∴ 2.6 cc. N/10 Ba(OH)₂ required for 5.134 gm. of fat.

∴ for 5 gm. 2.5 cc. will be required.

∴ Polenske (P.) number = 2.5.

Genuine butter fat gives a Reichert-Wollny number almost invariably over 24, and a minimum value of 20; it may be

as high as 40. The Polenske number of butter varies directly according to the Reichert-Wollny number, and it may be accepted that with no genuine butter fat does the P. number exceed that given in the table below.

R. W. No.	P. No.	R. W. No.	P. No.	R. W. No.	P. No.
20	2.1	25	2.6	29	3.4
21	2.2	26	2.8	30	3.5
22	2.3	27	2.9	31	3.7
23	2.4	28	3.2	32	4.0
24	2.5

Margarine, free from coconut oil, palm-kernel oil, and butter fat, will give R. W. and P. numbers in neither case exceeding 1.0, and usually about 0.5. Coconut oil gives an R.W. number 6.0 to 9.0, and a P. number 15.0 to 18.5; palm-kernel oil gives 5 and 9 to 12 respectively.

From a consideration of these figures, it is seen that if the fat from a sample of butter yields an R.W. number less than 24, there is a strong suspicion of adulteration, and if less than 20, adulteration may be presumed. If the P. number exceeds the maximum for genuine butter fat, the presence of coconut or palm-kernel oil is indicated.

Margarine fat giving an R.W. number over 1, either contains (a) butter fat, (b) coconut or palm-kernel oil, or (c) mixtures of the foregoing. In the first case (a) if more than 10 per cent. of butter fat (the maximum amount permitted) is present, the R.W. number will exceed 4. In the second case (b) the P. number will be more than 1, and in the third case (c) if the R.W. number is over 4, the presence of a proportion of coconut or palm-kernel oil will be apparent by the high P. number.

Where the test gives suspicion of adulteration, qualitative tests can be made as described below for the fat employed. It is an exceedingly difficult matter, in many cases, to detect adulteration in small proportion.

Cotton-seed Oil: Halphen's Test

It is to be noted that butter made from the milk of cows fed

on cotton-seed cake may give a slight reaction for this oil. The test fails if the oil has been hydrogenated ; it also reacts with Kapok oil.

Reagent.—1 gm. of sulphur is dissolved in 100 cc. of carbon disulphide, and to this is added 100 cc. of amyl alcohol.

About 4 cc. of the melted fat and an equal volume of the reagent are heated together for fifteen minutes, in a test tube, fitted with a long glass tube, placed in a boiling brine bath. A positive reaction is indicated by the production of an orange to deep red colour. In the absence of this colour it is well to add about 1 cc. more of the reagent, and to continue heating for a further ten minutes.

Sesame Oil: Tocher's Test

Reagent.—6.5 gm. of pyrogallie acid is dissolved in 100 cc. of concentrated hydrochloric acid.

15 cc. of the sample and an equal volume of the reagent are mixed in a small separating funnel. After standing about one minute, the acid portion is run into a large test tube, and boiled. A positive result is indicated by the solution giving a blue colour by reflected, and red by transmitted light.

In some countries it is legally enacted that margarine must contain a percentage of sesame oil in order that the adulteration of butter with margarine may be readily detected.

Preservatives

Butter and margarine very frequently contain preservatives ; those generally employed are boron compounds.

For the detection of preservatives, about 50 gm. of the sample is shaken in a separator, with about 30 cc. of water at 50° to 55° C., and the aqueous portion is separated, and examined by the tests given under milk (pages 138-141) ; it is to be noted that in the Hehner test for formalin it is necessary to add a small quantity of pure milk. Boron compounds when not exceeding

0.5 per cent. calculated as H_3BO_3 cannot be considered adulterants.

Estimation of Boron Compounds: Richmond and Harrison's Method ¹

25 gm. of the sample is just melted in a separator, and 25 cc. of warm water is added. The whole is thoroughly mixed, allowed to settle, again mixed, and after the second settling, 20 cc. of the aqueous portion is run out. In this the boron compounds are determined by the method of Richmond and Miller, described under cream (page 154).

For the calculation of the percentage of boron compounds the quantity of water in the original sample must be known.

EXAMPLE :

20 cc. of the aqueous portion requires 12.3 cc. N/10 sodium hydroxide. The sample contains 14.61 per cent. of water. Total quantity of water present with 25 gm. of sample in test $= 25 + \left(14.61 \times \frac{25}{100} \right) = 25 + 3.65 = 28.65$ cc.

Now 1 cc. N/10 sodium hydroxide $= 0.0062$ gm. H_3BO_3 , \therefore 12.3 cc. $= 0.07626$ gm.

There is 0.07626 gm. H_3BO_3 in 20 cc. aqueous portion.

\therefore there is $0.07626 \text{ gm.} \times \frac{28.65}{20} = 0.10924$ gm. in total aqueous portion, that is 0.10924 gm. in 25 gm. of sample $= 0.4369$ in 100 gm.

Boron compounds as boric acid $= 0.44$ per cent.

Artificial Colouring Matter

Butter and margarine are almost always coloured. Tests for the substances commonly used are given under milk (page 141).

¹ *Dairy Chemistry*, by H. Droop Richmond, 1914, p. 312.

LARD AND CHEESE

LARD

LARD is the refined fat of the hog, separated from the tissue by melting and subsequent draining; the process is known as 'rendering.' Several qualities, depending upon the parts of the carcass from which the fat has been obtained and the temperature employed in rendering, are sold under various designations. The best is that known as 'leaf lard.' 'Compound lard' is a mixture of lard and other fats, animal or vegetable, in various proportions; in some samples indeed lard has been entirely absent. The adulteration of lard consists in such mixtures being sold as pure lard, and in the admixture of water. Paraffin has also been used for hardening. The total extraneous matter, including water, should not exceed 1 per cent., and the colour should be pure white.

Water

Water is determined as in butter.

Foreign Fats

The fat is examined by the Reichert-Wollny-Polenske process. The Reichert-Wollny and Polenske numbers should in neither case exceed 1.0, and are generally about 0.5. High numbers indicate the presence of coconut or palm-kernel oil.

Tests may be made for cotton-seed and sesame oils. It is to be noted that the fat from animals fed on cotton-seed or sesame cake may give slight positive reactions with the appropriate tests. Beef stearin is very difficult to detect.

Paraffin

The presence of paraffin is indicated if a clear solution is not obtained on saponification in the Reichert-Wollny-Polenske test.

Reagents required :

Alcohol, absolute.

50 per cent. sodium hydroxide solution.

Petroleum ether.

Process : ¹

2 gm. of the fat, 2 cc. of sodium hydroxide solution, and 10 cc. of alcohol, are heated in a small flask under a reflux condenser, over a steam bath for one hour. The condenser is removed, and the alcohol evaporated; this may be considerably hastened by blowing air through the flask. The residue is thoroughly treated with 40 cc. of boiling water to dissolve all soluble matter. The solution, made cold, is poured into a separator, and the flask washed out into this with about 10 cc. of water. 20 cc. of petroleum ether is added; the whole is gently shaken, and allowed to settle. The lower layer is run into a small beaker, and the clear petroleum ether solution into a weighed flask. The aqueous solution of soap is returned to the separator, and three more similar extractions are given to remove the paraffin. The petroleum ether is distilled from the flask, and the latter with the residue is heated in the steam oven until constant in weight. Calculation to percentage is made in the usual way.

CHEESE

The varieties of cheese are very numerous, but the general principles of manufacture are the same. Milk or cream, generally from the cow, but in some cases from other animals, is allowed to sour naturally, or is coagulated with rennet, and the curd is separated from the whey. The curd, after the development of the proper degree of acidity, is salted, coloured in many kinds, pressed, and put aside to ripen. Soft cheeses are prepared by coagulating at a low temperature; hard cheeses require a higher temperature and considerably more pressure.

Cheese consists of protein, fat, water, mineral matter, and very frequently a small quantity of lactose. The percentage composition is subject to great variation.

¹ U.S. Department of Agriculture, Division of Chemistry, Bull. 65.

The adulteration of cheese is practised by using skim milk, and the fat deficiency is sometimes repaired by the incorporation of margarine and lard; these are called 'filled cheeses.' There is no legal standard for cheese.

In sampling cheese, pieces are taken out in several places by the well-known instrument designed for this purpose. The rind is removed, and the remainder cut up and thoroughly mixed.

Water

5 gm. in a basin, is dried in a steam oven until constant in weight.

Ash

The residue from the determination of water is ignited.

Protein

2 gm. is treated by the Kjeldahl process, and the total nitrogen found multiplied by 6.38.

Fat

Werner-Schmidt Method.—2.5 gm. of the sample is transferred to a Stokes' tube, and 5 cc. of water and 10 cc. of concentrated hydrochloric acid is added. The whole is heated and constantly shaken. After making cold, ether is added, and the fat extracted as in milk (page 130).

Short's Method.—2.5 gm. of the sample is intimately mixed with 5 gm. of anhydrous copper sulphate, by grinding in a mortar, and the mixture is transferred to a Soxhlet thimble. To the mortar, a little more of the copper sulphate is added, ground, and also transferred to the thimble. The fat is extracted in a Soxhlet apparatus (page 132), with ether which has been used to rinse the mortar and pestle.

Examination of the Fat

About 50 gm. of the sample in small pieces is tied in muslin and suspended in a beaker in a steam oven. The melted fat drops into the bottom of the beaker, and is given further heating, if necessary, to remove water. 5 gm. of this is used for a Reichert-Wollny-Polenske test (page 160), to determine

whether it is genuine butter fat. It must be noted that the fat may have undergone change, and the same limits cannot be so definitely presumed as in the case of fat from butter.

Detection of Adulteration

The Reichert-Wollny and Polenske numbers will give indication of 'filled cheese' by revealing the presence of foreign fats. Skim milk cheese is detected by the protein being markedly greater than the fat.

CARBOHYDRATES

THE carbohydrates are compounds of carbon, hydrogen, and oxygen. They include the starches and sugars, are widely distributed in the vegetable kingdom, and play an important part in animal metabolism. The starches have been shown to have the general formula $(C_6H_{10}O_5)_x$ and they may be regarded as complexes of sugar molecules $C_6H_{12}O_6$ after elimination of molecules of water.

The sugars are compounds of straight chains of carbon atoms which carry hydrogen atoms, hydroxyl groups, and one aldehyde or ketone group. The simplest sugars consist each of one single chain; others contain two or more chain groups combined through oxygen atoms. On hydrolysis, these complex sugars break, at the oxygen bonds, with addition of the elements of corresponding molecules of water, and are resolved into single chain sugars.

Nomenclature of Carbohydrates

The number of carbon atoms in the single chain is indicated by the prefix to the stem 'ose.' In the majority of the natural sugars this number is six, and therefore these are termed hexoses.

The sugars are further classified according to the number of chain groups combined in the molecule. Thus the single chain sugars are monosaccharides; those consisting of two groups are disaccharides; and of three, trisaccharides, etc.; the starches and celluloses fall under the head of polysaccharides.

Distribution and Uses of the Carbohydrates

From grain and tubers, starch is obtained as microscopic granules surrounded by a protective covering of cellulose. As the skin is insoluble in water, the starch does not dissolve until this is broken.

The starches of the different cereals, etc., differ mainly in their microscopical characteristics, and the microscope is the

chief authority for their identification and the detection of their admixture (see Figs. 32 to 45).

The foodstuff cereals include wheat, maize, rye, oats, barley, rice, etc., of which wheat gives the high-grade flour of this country. Maize is popular in America, and is finding an increasing market in Europe. Rye has almost disappeared from this country, but is still largely used on the continent.

The cereal grains contain naturally occurring enzymes, including diastase, which develop under suitable conditions of moisture and germination, and convert starch, after it has been rendered soluble by other enzymes or by heat, into maltose and dextrin. In this way starch is hydrolysed into sugars available for fermentation, etc. The first stage in the assimilation of starch consumed as food is its hydrolysis into sugars by means of the diastase in the saliva.

Sugars occur naturally in the sugar-cane, sugar-beet, maple, fruit, milk, honey, etc. Starch sugar (sugar manufactured from starch) is extensively employed in food mixtures, confectionery, and as a substitute for, and an adulterant of, natural sugars. When sold as a substitute for naturally occurring sugars, it should be marked by some fancyname not suggestive of a natural source. In recent years starch syrup has been sold under a variety of misleading names carefully chosen to imply a natural origin.

The syrup separated in the crystallisation of table sugar contains about 25 per cent. of sucrose which is prevented from crystallising by the large amount of glucose and fructose present. The syrup is used under the name of golden syrup or treacle.

Jams, in addition to the sugar of the fruit, contain sugars added in the preparation. Honey consists of a mixture of glucose and fructose. Milk is characterised by the presence of lactose (milk sugar).

By fermentation the monosaccharides are converted into alcohol and carbon dioxide, and the polysaccharides undergo the same decomposition after hydrolysis to monosaccharides. These reactions are the basis of the manufacture of alcoholic liquors from grain and other starchy matters, and from the juices of fruits.

Alcohol is oxidised in contact with air, by means of a micro-organism into acetic acid. By this means beer, wine, grain and fruit juices are converted into vinegar.

FLOUR

Flour is the interior of the wheat grain ground very finely. It is obtained by a process of conditioning and grinding, and separation of the bran, germ, and fibre by sieving or air draught. The wheat yields about 70 per cent. of pure flour. The modern steel roller mills, in addition to purification from the fibre, separate the flour itself into grades representing various layers of the grains. Some processes aim at a minimum separation of bran and germ, and produce the grades known as whole-meal and standard flours.

Natural, well-separated flour is white with a tinge of golden-yellow or, as it is known, 'bloom.' High grades show a uniform appearance, while lower grades are spotted with dark grey particles of germ and fibre. Some strong flours, as for example, Russian flour, are darker than others. Storage for one or two months after milling whitens, and improves the baking qualities of, the flour, but longer storage causes deterioration and increases acidity.

The following analyses show the average percentage composition of wheat grain and of the flour and bran obtained therefrom.

	Wheat	Flour	Bran
Water	14.5	14.2	11.9
Carbohydrates	62.2	67.4	51.7
Protein	14.9	14.6	15.8
Fat	2.1	1.3	3.8
Fibre	3.8	1.5	8.7
Ash	2.3	0.8	7.5
Acidity as lactic acid	0.12	0.08	0.23

The composition of flour, in addition to natural fluctuation, varies according to the extent of bran separation, and may serve to indicate the grade of the flour. Flour may be, moreover, subject to elaborate and scientific adulteration and conditioning. The aim of these is to increase weight by admixture with foreign starches, etc.; to increase the strength by the addition of so-called 'improvers'; and to enhance the whiteness and uniformity of appearance by means of bleaching. The baking value of flour depends on its 'strength,' that is, its ability to produce a large-volumed well-risen loaf, and also

on its water-absorbing capacity. The strength of a flour appears to be proportionate to the amount of gluten which it contains, and the percentage of gluten affords a rough but not a reliable gauge of the strength.

Many chemicals, some of them of a highly dangerous nature, have been used at different times as improvers. They are usually added by atomising aqueous solutions into the flour. The most common improvers are alum, copper sulphate, phosphoric acid and its acid salts. The addition of phosphates has been defended as being advantageous in view of their nutritive value; this is only true of phosphorus in organic combination, in which form it is usually present when occurring naturally in foods.

The bleaching of roller-mill flour originated in this country about 1906, and has since become general. Several bleaching agents have been employed, such as ozone, chlorine, oxides of chlorine, bromine, and oxides of nitrogen, of which the last is most commonly used. The amount of nitric peroxide in the air, with which the flour is treated, averages 40 to 100 parts per million, and the amount used to bleach 1 kilo. of flour varies from 3 to 50 cc. The nitric peroxide absorbed reacts quantitatively with test reagents for nitrites.

The natural variations in composition of good grade flour are sufficiently small to be immaterial, and the public health analyst is chiefly interested in possible weighting with foreign starches, mineral matter, and water, and in bleaching, improvers, and moulds. Some of the more variable constituents, however, may be estimated as an indication of the grading of the flour. Adulteration is readily detected by microscopical examination. Chemical tests for potato starch have not been found reliable. The full analysis falls into the following divisions:

(1) Microscopical examination for foreign starches, fibre, germ, and ergot.

(2) Chemical examination for bleaching, improvers, other adulteration, and ergot.

(3) Analysis for normal constituents.

The following is the desiderata for a wholesome flour:

Moisture.—Not exceeding 15 per cent.

Protein.—Estimated as nitrogen, not less than 1.5 per cent.

Fat.—1.5 per cent. High values show incomplete removal of germ during milling.

Acidity.—Calculated as lactic acid, not exceeding 0.25 per cent.

Ash.—Over 1 per cent. indicates low-grade flour or mineral adulteration.

Nitrites.—Not exceeding 0.7 parts, calculated as NO_2 , per million.

MOISTURE

Process.—10 gm. of the flour is weighed into a porcelain dish and heated at 100°C . until constant in weight; two to three hours are required. The loss in weight represents moisture.

PROTEIN: KJELDAHL-GUNNING METHOD

The protein in flour is estimated as nitrogen; a close approximation of the protein in cereals is obtained by multiplying the nitrogen by 6.25.

Reagents required:

Sulphuric acid, concentrated, nitrogen-free.

Sodium sulphate, pure dry powdered.

Sodium hydroxide solution, 40 per cent.

N/10 sulphuric acid.

N/10 sodium hydroxide.

Process:

The nitrogen of the protein is converted into ammonium sulphate, and the ammonia is estimated; from this the nitrogen is calculated.

1 gm. of flour is placed in a dry Kjeldahl flask—a round-bottom hard-glass flask, with a long neck, and of about 250 cc. capacity. 30 cc. of concentrated sulphuric acid and 8 gm. of sodium sulphate are added, and the flask, placed in an inclined position on a metal stand, is heated directly with a small bunsen flame. During carbonisation frothing takes place, and heating must be gentle until this has subsided. The flame is then raised to bring the acid to boiling. When the liquid has become clear and decolorised it is allowed to cool gently. It is then transferred to a litre flask, 200 to 300 cc. of distilled water being used to wash it from the one flask to

the other. The distillation of the ammonia is now proceeded with as follows.

This flask is placed on a tripod and gauze, and is closed with a rubber stopper carrying a tap funnel, and an outlet tube provided with a splash trap bulb. The outlet tube is a double right-angled bend, and passes into the top of a vertical, double-surface condenser. An efficient splash trap device may be provided by making a series of rectangular bends stepwise from the flask to the condenser. The lower end of the condenser passes into a rubber stopper fitting into the wide neck of a receiving jar or flask; it does not pass into the liquid in the jar. The stopper of the receiver further carries an outlet tube sealed into a wide tube of about $\frac{1}{2}$ -inch diameter and 3 to 4 inches long, which is filled with glass beads. After connecting the distilling flask with the condenser, the tap funnel is opened to allow exit of air, and 50 cc. of N/10 sulphuric acid is run, from a pipette, through the beaded exit into the receiver. 150 cc. of 40 per cent. sodium hydroxide solution, previously boiled with a pinch of zinc dust, is now placed in the tap funnel and added gradually without allowing the flask to be open to the air. The contents of the flask are then distilled until 200 to 250 cc. of distillate has been collected in the receiving jar. The distilling flask is then disconnected, and the condenser and bead tube are rinsed into the receiver with several washings. After removing the stopper of the receiver, the contents are titrated with N/10 sodium hydroxide, using methyl orange as indicator. The deficiency of decinormal alkali required represents the ammonia distilled over, and from this the nitrogen in the sample is calculated; each cc. = 0.0014 gm. nitrogen.

EXAMPLE :

Weight of sample used = 1.0000 gm.

N/10 sulphuric acid placed in receiving flask = 50.0 cc.

N/10 sodium hydroxide required to neutralise sulphuric acid remaining = 37.7 cc.

$\therefore 50 - 37.7 = 12.3$ cc. N/10 sulphuric acid has been neutralised by ammonia.

1 cc. N/10 acid = 0.0017 gm. NH_3 = 0.0014 gm. nitrogen.

12.3 cc. N/10 acid = 0.01722 gm. of nitrogen.

\therefore Nitrogen in flour = 1.72 per cent.

Protein = $1.72 \times 6.25 = 10.75$ per cent.

FAT

10 gm. of the flour is dried at 100° C. for two to three hours, and extracted with dry ether in a Soxhlet.

GLUTEN

50 gm. of flour, made into a stiff dough, is wrapped in a bag of fine muslin cloth. The bag is placed in a stream of water, and gently pressed with the fingers until all the starch has been washed out and the water runs away clear. The gluten which remains is transferred to a dish, dried at 100° C., and weighed.

ACIDITY

10 gm. of the flour is weighed into a conical flask, and covered with 100 cc. of boiled water. The flask is stoppered and allowed to stand, with occasional shaking, for one hour. The contents are then titrated with N/10 sodium hydroxide, using phenolphthalein as indicator.

EXAMPLE :

10 gm. flour required, 1.9 cc. N/10 NaOH.

1 cc. N/10 NaOH = 0.009 gm. of lactic acid.

∴ 2.9 cc. N/10 NaOH = 0.0171 gm. lactic acid.

Acidity of flour, calculated as lactic acid = 0.17 per cent.

AQUEOUS EXTRACT

Cold water extracts sugar, dextrin, vegetable albumen, and soluble salts from flour.

Process :

20 to 50 gm. of the flour is occasionally shaken for two hours in a bottle with 200 to 300 cc. of water. To estimate the extracted solids, the solution is evaporated to dryness in a porcelain basin on a steam bath, and the residue is weighed; it is then ignited, and the ash, which should consist entirely of potassium phosphate, is weighed. The presence of other mineral matter in the ash of the cold-water extract is an indication of adulteration, and requires further investigation.

The soluble phosphate bears a variable relationship to the total phosphates in the flour, but is always greater than one-half. The residue is taken up with water, and titrated with standard uranium acetate solution. 6 gm. of uranium acetate is dissolved in water, 5 cc. of glacial acetic acid is added, and the whole is diluted to 1 litre. The solution is standardised against a standard solution of sodium ammonium hydrogen phosphate containing 2.9441 gm. microcosmic salt per litre, which corresponds to 0.001 gm. P_2O_5 per cc. The uranium acetate is delivered, from a burette, into 25 cc. of the standard phosphate solution, until a drop, extracted on a rod, gives a buff, orange, or red coloration with potassium ferrocyanide solution, thus showing an excess of uranium salt. The uranium acetate solution is then diluted so that 1 cc. corresponds to 0.001 gm. P_2O_5 .

EXAMPLE :

Extract and Ash of Extract

25 gm. gave 0.951 gm. of extract.

∴ extracted solids = 3.804 per cent.

On ignition the residue was 0.103 gm.

∴ Ash = 0.412 per cent.

Soluble Phosphates

Ash from above, dissolved in water, required 5.7 cc. standard uranium acetate solution.

1 cc. standard uranium acetate solution = 0.001 gm. P_2O_5 .

∴ 5.3 cc. = 0.0053 gm. P_2O_5 .

0.0053 gm. P_2O_5 in 25 gm. of sample = 0.212 per cent. soluble phosphates.

ASH

10 gm. of the flour is weighed into a shallow basin, and ignited. The decarbonisation can be accelerated by the addition of 1 to 2 gm. of ammonium nitrate, but in this case the ammonium nitrate must be tested in a blank experiment for non-volatile matter; its use is not recommended for accurate work.

A high value suggests mineral admixture which must be confirmed by analysis of the ash. The total phosphates may be determined in the ash, by the method given above, after solution in dilute acetic acid.

DETECTION OF NITRIC PEROXIDE BLEACHING

5 gm. of the sample is macerated in a porcelain mortar with 100 cc. of pure water. The mortar must be free from nitrites, and it is advisable that no bunsens be burning in the vicinity. The mixture is filtered, and the filtrate tested for nitrites as described on page 78; 1 cc. of the standard potassium nitrite solution = 0.0328 mgm. NO_2 . The results are conveniently expressed as parts of NO_2 per million.

Unbleached flour frequently absorbs nitrites from the air, especially in industrial towns, but the amount is well within 0.70 parts NO_2 per million, and for practical purposes this can be accepted as the limit for unbleached flour. It is important to note that during storage a decrease in nitrites may occur with a corresponding increase in nitrates.

DETECTION OF IMPROVERS

A sample of the flour is shaken with chloroform; the starch granules rise to the surface, while heavy mineral matter settles to the bottom and if crystalline may be recognised by the aid of a microscope or pocket lens, or it may be separated for further examination.

Alum

Solutions required:

A fresh extract of logwood. About 1 gm. is shaken in a test tube with a small quantity of alcohol and the extract decanted.

Saturated solution of ammonium carbonate.

Process:

A mixture of 10 cc. of each of these solutions is diluted with water to 150 cc. 50 gm. of flour is macerated in a mortar with 100 cc. of water, and four or five drops of the freshly prepared diluted logwood solution are added. In the presence of alum, exceeding one part per 10,000, a blue-lake develops on standing; pure flour gives a pink coloration.

The logwood test reacts only with aluminium salts in solution, and no blue coloration is produced by the aluminium normally present in flour as silicate. Thus aluminium, shown

by the logwood test, is present as soluble salt, and has been artificially added. The alumina normally present in a pure flour bears a fairly constant relationship to the silica present, such that the silica approximately equals the alumina calculated as alum. Thus it is customary to calculate alumina as alum, and to allow a quantity equal to that of the silica present; alum above this amount is regarded as added adulteration, subject to confirmation by the logwood test. The estimation of alum may be carried out by analysis of the soluble extract, together with an examination of the total alumina in the ash of the flour.

Persulphates

A sensitive colour reaction for persulphates is given with a 2 per cent. solution of benzidine in alcohol, and is capable of detecting one part per million. To apply this to flour, 20 gm. of the sample is extracted with 100 cc. of water, and filtered. 10 cc. of benzidine solution is added; a blue colour is formed with dilute solutions of persulphates (yellow with concentrated solutions).

Phosphates

Phosphate improvers are detected by abnormal phosphates in the ash and in the soluble extract; when they are suspected, an analysis of the ash of the flour is essential.

Copper Salts

Copper salts can be readily perceived by the red coloration imparted, to the sample of flour, by a solution of potassium ferrocyanide acidified. If suspected in quantity, copper is estimated in the ash of the flour (page 269).

ERGOT AND MILDEW

A microscopical examination for ergot in flour may be necessary. Ergot may be revealed by the development of a fungus taint on storing a moistened sample of the flour in a stoppered bottle at 30° C. for twelve hours. A further test is to extract 10 gm. of the flour with 100 cc. of boiling alcohol,



Fig. 30.—Ergot of Rye (*Claviceps purpurea*). ($\times 80$.)



Fig. 31.—Mildew on Stem of Wheat (*Puccinia graminis*). ($\times 100$.)

to decant the alcohol, and to acidify with dilute hydrochloric acid; a red coloration indicates ergot, and a purple coloration is given with mildewed flour.

MICROSCOPICAL EXAMINATION

The microscopical examination of flour, by the characteristic appearance of its starch, will readily reveal the nature of the original cereal. Though the general microscopical examination of foodstuffs is a subject in itself, it is convenient to include in this volume some notes on the detection of starches by the microscope; the examination is easily made, and the results are of great utility for a variety of purposes.

When examining solid food products for starches, a minute quantity is placed on a slide, and a very small drop of glycerine is added to it. The two are incorporated by stirring with a glass rod, which has been drawn out fine and a small bead made. A cover glass is then dropped on and pressed right down; the quantity of glycerine used should be such that it does not exude from under the cover glass.

In examining the preparation under the microscope, a general survey is made under a low power (magnification about 120), and then selected fields are examined critically under a high power (magnification about 600 to 700). In using the lower power, the field should not be brightly illuminated, otherwise the translucent starch grains may not be noticed. Further information may be gained if the microscope fitting permits the use of polarised light.

While all the starches have their characteristic microscopic appearance, it must be borne in mind that frequently only a small proportion of the grains exhibit this, and sometimes a proportion deviate distinctly from the normal.

In the following figures, fourteen of the commonly occurring starches are illustrated; some of the clearness and sharp definition is lost in the photomicrographic process. As the size of the starch grain is one of the most important factors in identification, all the photographs have been taken at the same magnification (730), and are therefore strictly comparable.

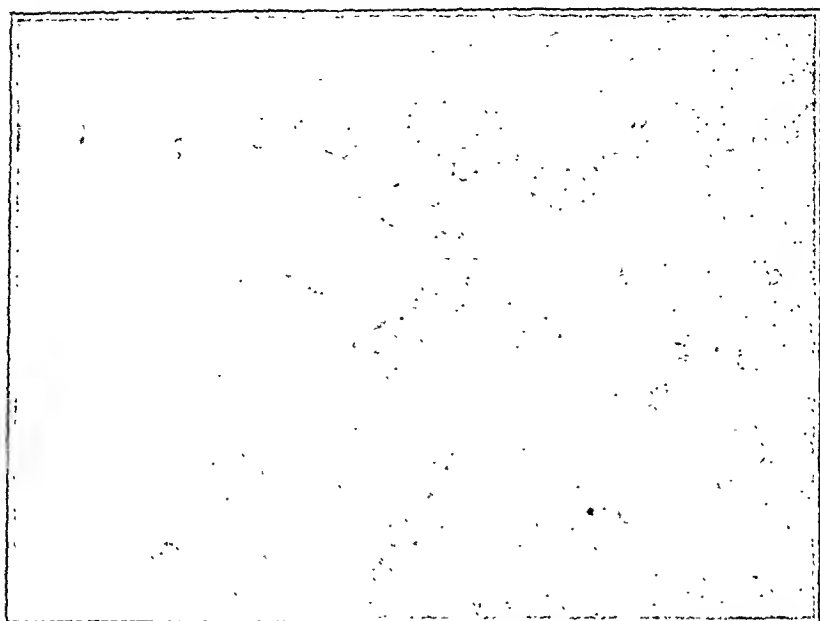


Fig. 32.—Rice Starch. ($\times 730$).

Polygonal in shape, having generally five or six sides; angular aggregations are common. The grains have a diameter of 3 to 7μ . The hilum is central, but is frequently not observed (seen in bottom-centre of field above).

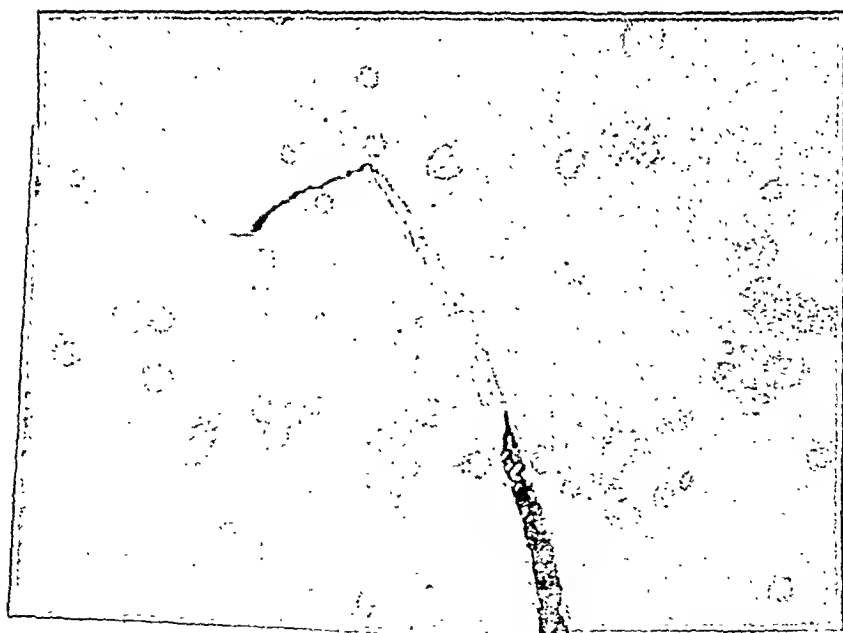


Fig. 33.—Buckwheat Starch. ($\times 730$.)

Both polyhedral and rounded in shape; aggregations of three to ten grains are very characteristic (seen in bottom-left of field). The grains have a diameter of from 3 to 13μ . The hilum is central and distinct.

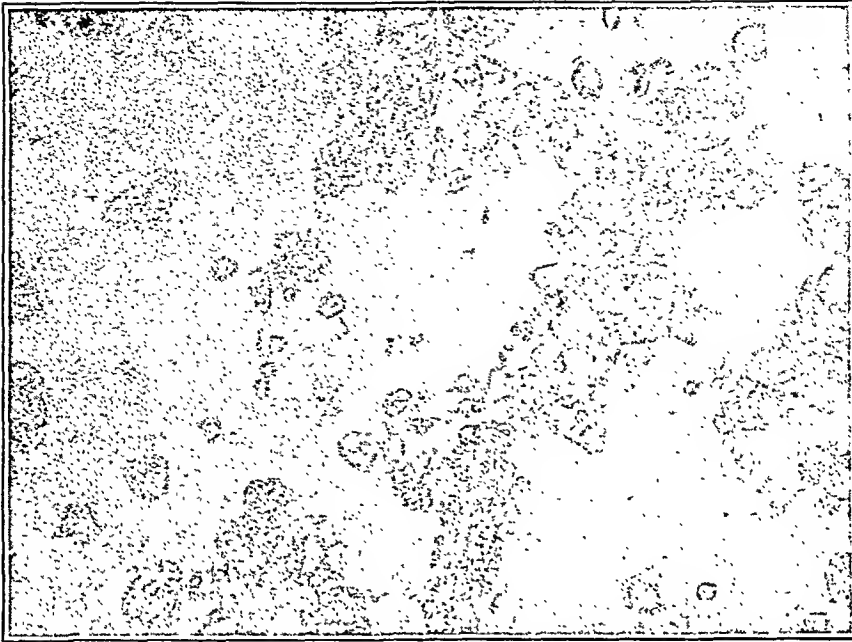


Fig. 34.—Oat Starch. ($\times 730$.)

Angular and rounded in shape, with coherence in aggregates; compound grains, invariably rounded, generally oval, and with interstices, are characteristic. The grains themselves have a diameter of 4 to 9μ , and the compound grains 25 to 45μ . (Seen in field above, to right near top and to left near bottom from central vertical line.) No hilum is evident.

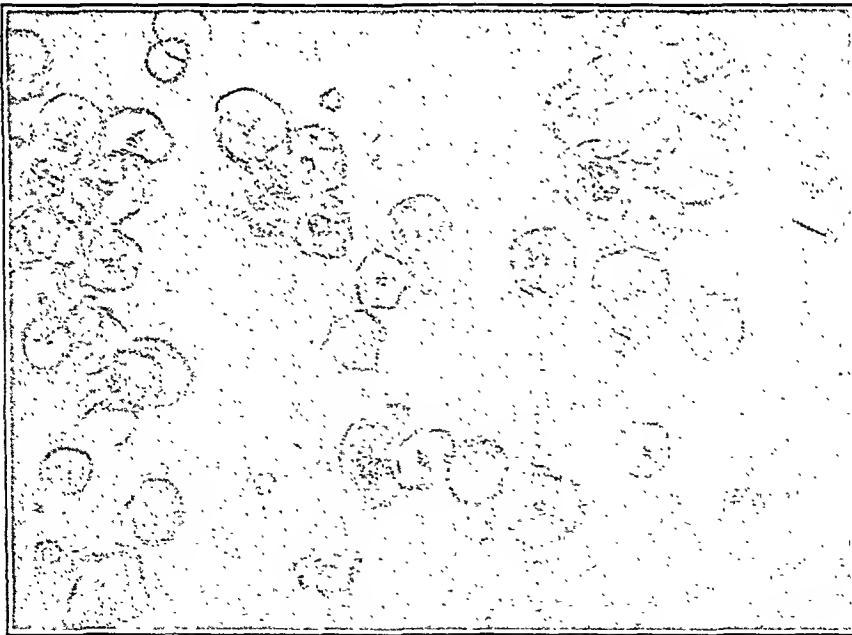


Fig. 35.—Maize Starch (Indian Corn). ($\times 730$.)

Polygonal and rounded in shape; aggregations are common. The grains have a diameter of 11 to 22μ . The hilum is more or less central, very distinct, and sometimes linear and stellate in form.

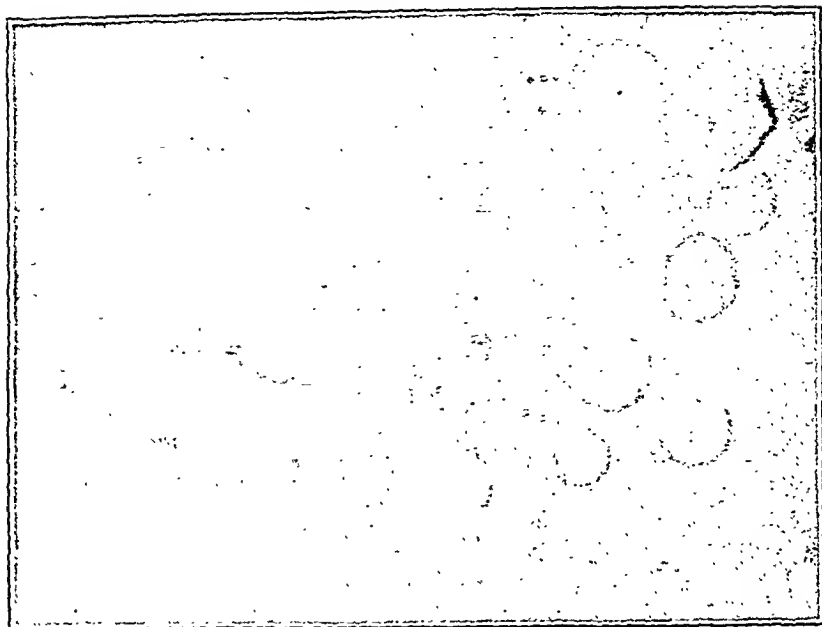


Fig. 36.—Tapioca Starch (*Cassava*, *Manioca*). ($\times 730$.)
Rounded and kettledrum in shape; diameter 12 to 26 μ . The hilum is central and very distinct.

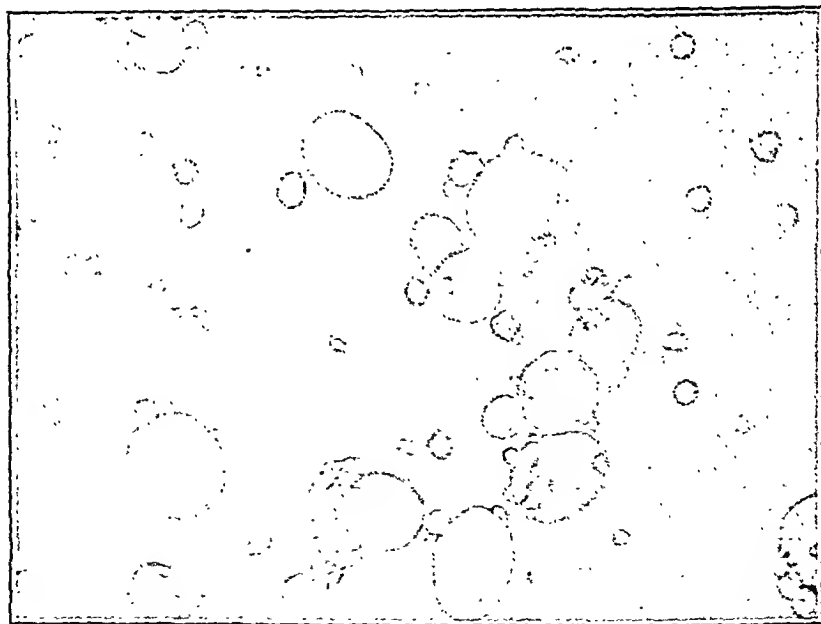


Fig. 37.—Wheat Starch. ($\times 730$.)

Rounded, roughly circular in shape, with large grains 22 to 40 μ , and small grains, 2 to 6 μ in diameter, with very few intermediate sizes. The hilum is central, but generally is observed only in the small grains. The general characters are very similar to those of barley starch, but it is distinguishable by the following differences: (a) the small wheat grains are considerably larger than the small grains of barley; (b) the wheat grains are more translucent; (c) the attachment to, and superimposition of, the small grains on the large grains is much more general than in the case of barley.

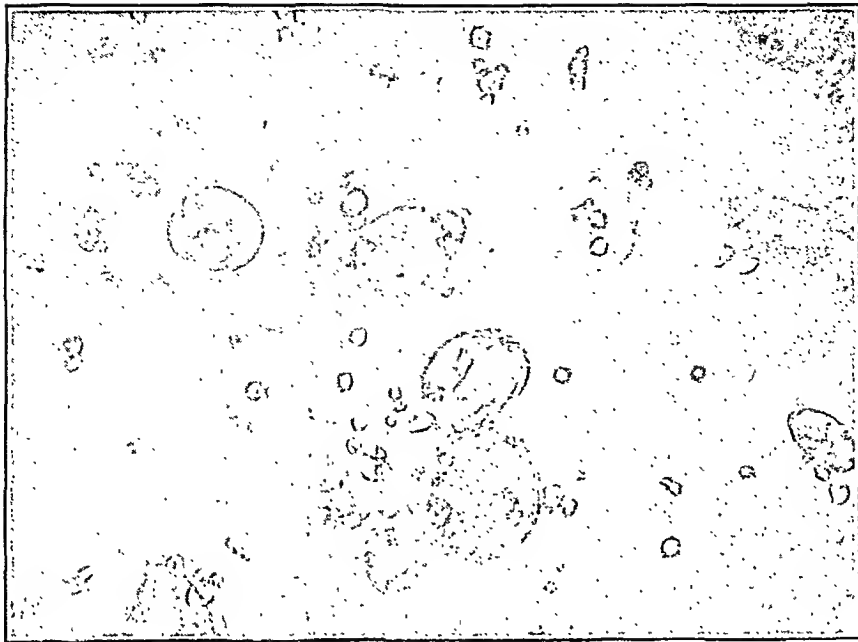


Fig. 38.—Barley Starch. ($\times 730$.)

Rounded, roughly circular in shape, with large grains 20 to 38μ , and small grains 0.5 to 3μ in diameter, with very few intermediate sizes. A hilum is generally only observed in the small grains. The general characters are very similar to those of wheat starch, but it is distinguished by the differences given above.

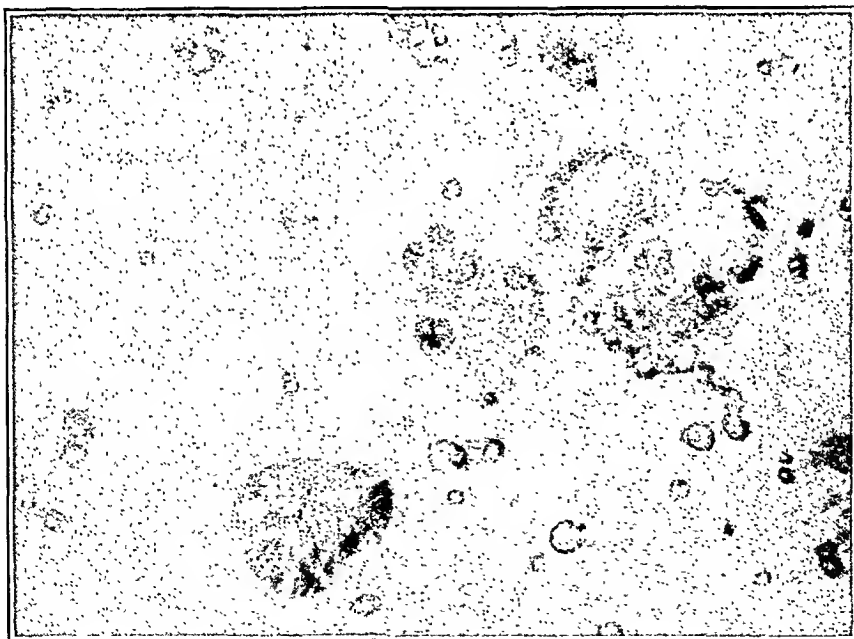


Fig. 39.—Rye Starch. ($\times 730$.)

Somewhat similar in appearance to wheat and barley starch, but the larger grains have greater dimensions than those of the foregoing; they have a diameter of 22 to 48μ , and a rayed hilum may be observed (seen in large grain in bottom-left of field above).

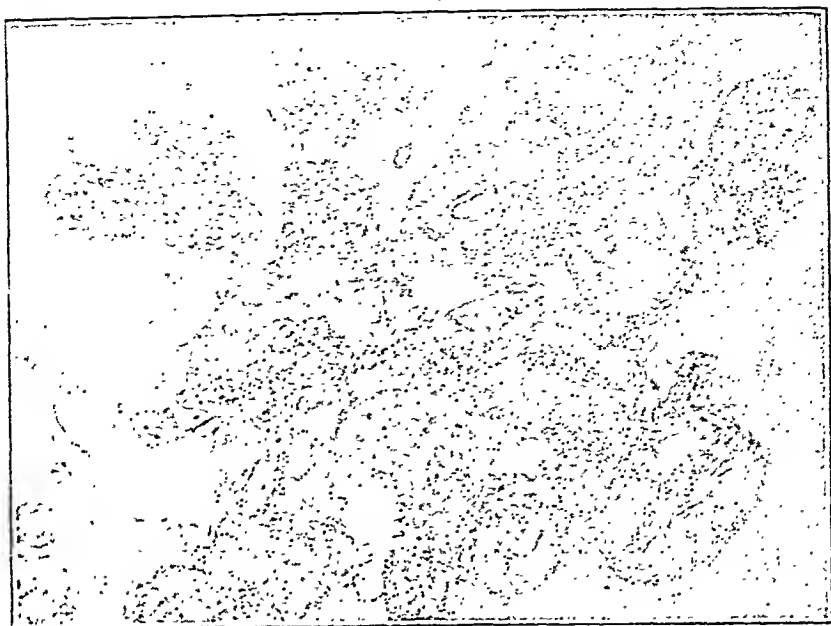


Fig. 40.—Pea Starch. ($\times 730$.)

Rounded kidney shape. The long diameter varies from 17 to 35μ . The hilum is very distinct, appearing as a puckered slit running in the long axis. Notches cutting into the outside edge are common. The grains are sometimes fractured. They are very similar to those of the bean, but are distinguished from the latter by being rather smaller, and more uniformly ellipsoidal in shape; circular forms are rare, very few grains have a branching cleft, and concentric rings may be observed. (Cf. large grain extreme right-bottom of field with large grain centre-bottom in field below.)

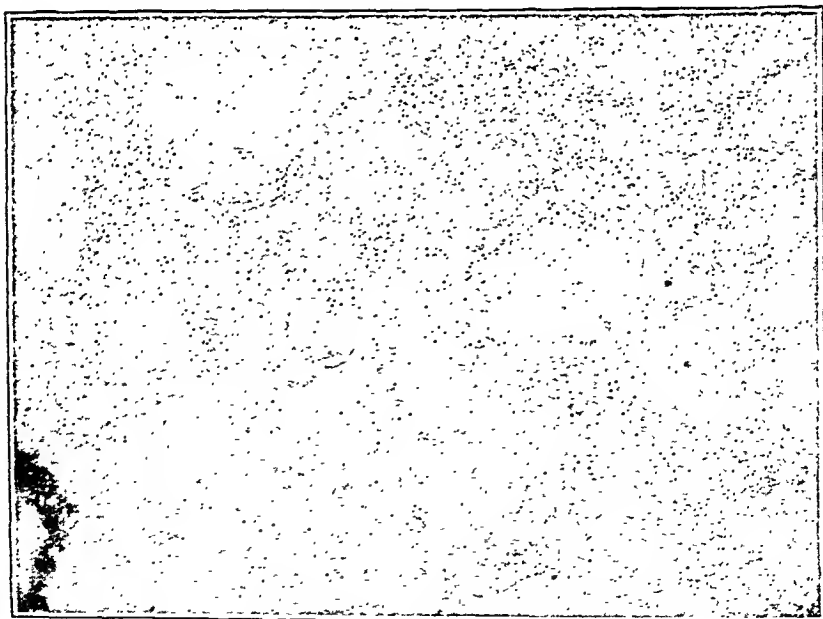


Fig. 41.—Haricot Bean Starch. ($\times 730$.)

Rounded, kidney-shaped, but more circular forms are common. The long diameter varies from 17 to 45μ . The hilum is very distinct, appearing as a puckered slit running in the long axis with frequently a cleft branching at right angles. Concentric rings are very seldom seen. The general appearance is very similar to that of pea, from which it can be distinguished by the differences given above.

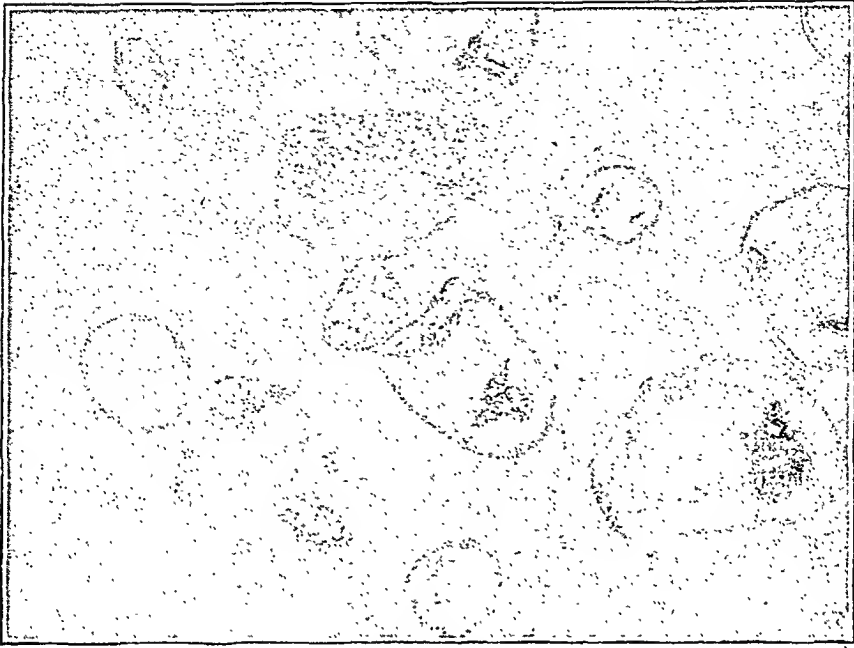


Fig. 42.—Sago Starch. ($\times 730$.)

Irregular, elongated in shape, rounded at one end (commonly the broadest) and truncated at the other. The larger grains are 28 to 70μ long. The hilum is eccentric and very marked, appearing as a star, slit, or irregular formation.

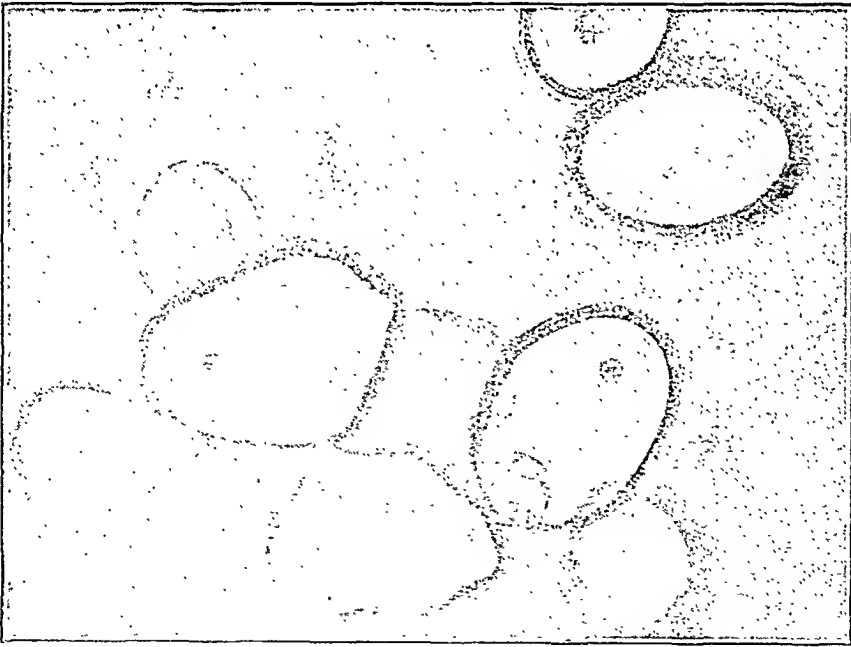


Fig. 43.—Potato Starch. ($\times 730$.)

Ellipsoidal and oyster shell in shape. Large grains are 40 to 95μ long. The hilum is eccentric, very distinct, and is generally situated at the *narrow* end. Concentric rings may be observed.

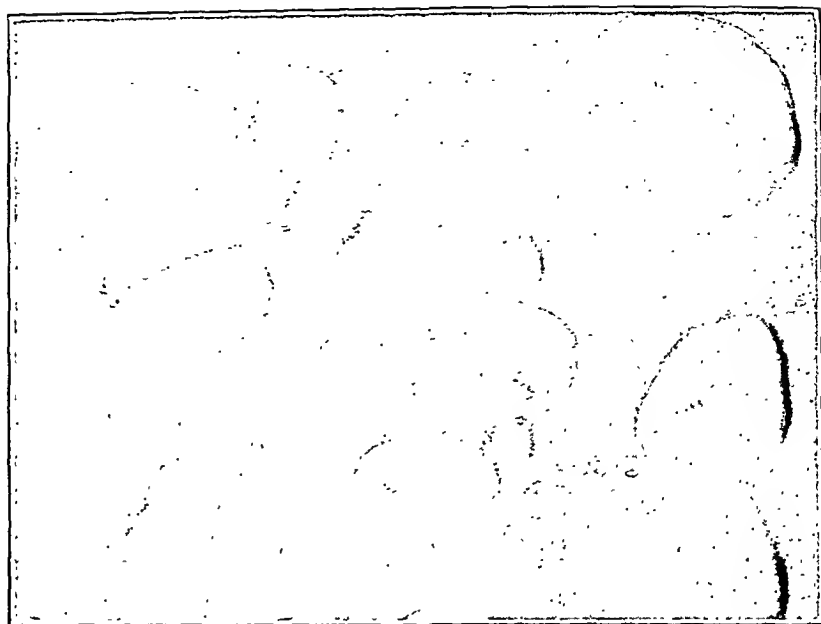


Fig. 44.—West Indian Arrowroot Starch (Maranta Arrowroot.) ($\times 730$.)

Ellipsoidal, oyster shell, and flattened ovoid in shape. Large grains are 30 to 75 μ long. The hilum is eccentric, very distinct, and is generally situated at the broad end. Concentric rings may be seen.

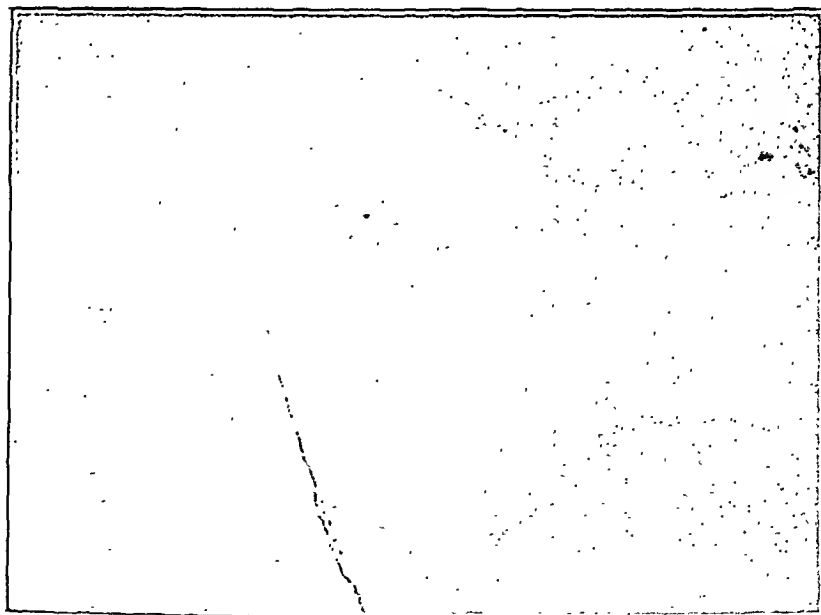


Fig. 45.

Australian Arrowroot Starch (*Toum les mois*, Canna Arrowroot). ($\times 730$.)

Ovate in shape, and in some cases, more or less pointed at one end. The grains have a length of 47 to 132 μ ; it is the largest of the commoner occurring starches. The hilum is not very distinct, is eccentric, and situated at the narrow end. Concentric rings are very distinct and regular. While the shape is similar to that of potato, distinction is easy on account of the greater size.

B R E A D

Bread is prepared by baking a paste of flour and water which, in order to increase its digestibility, has been made cellular by means of carbon dioxide, generated either from fermentation with added yeast or from added baking powder or, in the case of 'aerated' bread, from a high-pressure aqueous solution of carbon dioxide. Reduced pressure, by the use of vacuum ovens, has also been employed to cause the dough to rise during baking.

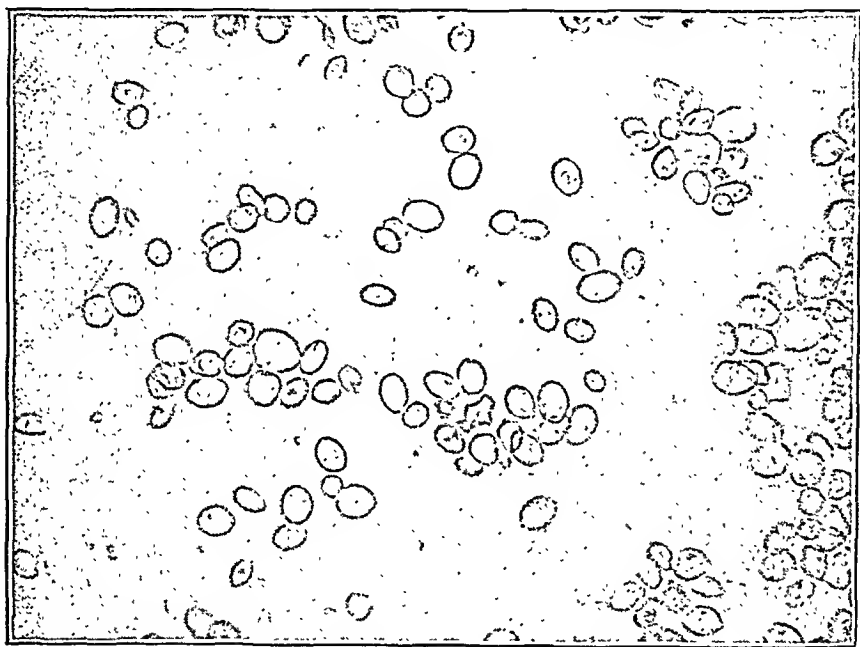


Fig. 46.—Yeast. ($\times 730$.)

The processes involved in bread-making with yeast, which, on account of the superior flavour imparted, is the most general method, are briefly as follows. As soon as the flour is wetted in the dough, the diastatic enzymes, present in the flour, render some of the starch soluble and convert this into maltose and dextrin; the added yeast hydrolyses the maltose into glucose, and ferments it during the subsequent warm standing, producing carbon dioxide. The extent to which the dough distends thereby depends upon the amount and elasticity of the gluten present. When the loaf has risen to its maximum (excessive

fermentation attacks the gluten and destroys its strength) it is baked, during which the excess of moisture is expelled and the gluten coagulates and fixes the porous structure of the bread.

These processes are much influenced by the nature of the constituents of the flour. Bran and germ have a high protein content, and flours to which they, especially the germ, have been added for the sake of their supposed, but questionable, nutritive value, are on the market. Bran and germ have greater diastatic activity than pure flour, and flour containing them gives clammy heavy loaves on account of the greater diastatic conversion of the starch, and weakening of the gluten. Moreover, they are less digestible and more liable to bread diseases, such as 'ropiness,' than pure flour bread. These disadvantages are said to be overcome by previously heating to destroy diastatic activity.

Bread diseases include the development of excessive acidity by lactic fermentation due to lactic ferments introduced with the yeast, and the semi-liquefaction known as ropiness. The latter is characterised by the formation of a viscous paste in the centre of the loaf, where the temperature has not been high. When the loaf is broken, the paste draws out in fine filaments which remain attached to the two parts. Ropiness has been traced to the presence of *B. Mesentericus* in the flour. It occurs for the most part in bread prepared from low-grade flour, damp bread, and bread low in natural acidity, and is almost unknown in bread from pure flour. During the war cases of bread disease were comparatively common due to the low-grade flour used.

The occurrence of staleness has been shown by Whymp¹ not to be due to the moisture condition, but rather to the texture of the bread, namely, to the deposition of solid starch from the crumb colloid, and to polymerisation of the starch. It is caused by underbaking, or by dryness of the dough, which prevents efficient gelatinisation of the starch; or by inferior viscultation due to weakness of the flour or yeast; incorrect mixing and baking of the dough; and irregular drying of the loaf. Any of these causes may prevent or destroy the full cellular formation of the bread.

¹ *The British Baker*, 1918.

Chemically, bread consists of flour and water, and little change of the constituents has been detected. That the starch does undergo a certain change is seen by the difference in its baking properties after successive bakings.

The quality of bread depends chiefly on that of the flour, and the adulteration and impurities of bread are generally those which existed in the flour; adulteration during baking is rare.

To obtain an average sample, one quarter of the loaf is reduced to small size, and mixed.

The analysis, which is carried out as for flour, includes the following estimations:—

Moisture.—Should not exceed 45 per cent.

Ash.—Should not exceed 1.4 per cent., of which not more than 0.2 per cent. should be soluble in dilute hydrochloric acid.

Improvers.—The test for improvers as in flour must show them to be absent.

Bleaching.—As for flour.

Starch.—Page 227.

Acidity

25 gm. of the sample, on a gauze filter, is washed with warm water, and the filtrate is titrated with N/10 sodium hydroxide, using phenolphthalein as indicator. The acidity is calculated to lactic acid: 1 cc. N/10 NaOH = 0.009 gm. lactic acid.

Salt

25 gm. of the sample is gently carbonised, cooled, extracted with warm water, filtered, and washed; the filtrate is titrated with N/10 silver nitrate (see page 70): 1 cc. N/10 AgNO₃ = 0.00585 gm. sodium chloride.

Addition of Foreign Starches

If this addition has taken place prior to baking, it is discovered by microscopical examination of the flour; if it is suspected at the hands of the baker, its detection in the finished bread can be effected only on general considerations, as the starch grains are completely changed in appearance during baking.

Addition of Improvers, etc.

The presence of makeweights and improvers is shown by the high percentage and composition of the ash of the bread. Salt is of course a normal addition during baking, and allowances must be made for the use of baking powder. Alum and copper sulphate may be added to impart whiteness to the finished loaf. The nitrite of bleached flour is partly oxidised to nitrate during baking, but sufficient remains unchanged to make the detection of this form of bleaching possible by the Lombard test.

THE PROPERTIES OF SUGARS

THE sugars exhibit the characteristic property of rotating, to a specific degree, the plane of polarisation of a beam of polarised light passing through a solution; this property is therefore utilised both for their detection and estimation.

Specific Rotation

The specific rotation is the rotation of the plane of polarisation of a polarised beam traversing through 1 decimetre of a solution containing 100 gm. of the sugar in 100 cc. Then

specific rotation $[\alpha] = \frac{R}{l \times p}$ when

p = grammes of sugar in 1 cc. of solution,

l = length of solution in decimetres,

R = rotation of polarised beam.

Specific rotations with sodium light are written $[\alpha]_D$, and with sunlight $[\alpha]_s$.

In some cases specific rotation varies appreciably with the temperature; it is also slightly influenced by concentration of the solution.

Rotation may be clockwise or anti-clockwise to the axis of propagation, and according as it is given to the right or to the left in the observing instrument, it is called *dextro* or *laevo* rotary, and written as positive or negative respectively.

Reducing Power

Many sugars reduce a number of metallic salts to lower oxides or to metals. Thus cupric oxide in alkaline solution is reduced to cuprous oxide, and the weight of cuprous oxide formed by a standard weight of a sugar affords a convenient measurement of its reducing power. Reducing powers are specific, and provide a means of estimation.

sucrose. Its reactions with acids and alkalies are similar to those of glucose.

Invert Sugar

Invert sugar is a mixture of equal amounts of glucose and fructose. It occurs commonly in nature, and is the product of the hydrolysis of sucrose. It derives its name from the fact that at ordinary temperatures the strongly laevo-rotary fructose imparts a laevo-rotation to the mixture; consequently the hydrolysis of sucrose, which is dextro-rotary, is accompanied by a change from dextro- to laevo-rotation, or inversion. The properties of invert sugar are those of glucose and fructose in equimolecular mixture, and the specific rotation is the mean of that of glucose and fructose.

DISACCHARIDES

Sucrose (Cane, Beet, or Table Sugar)

Sucrose is the principal ingredient of the products of the sugar cane, beet, and maple industries. Sucrose does not show reducing power. Concentrated sulphuric acid chars it vigorously, liberating pure carbon. It is very readily hydrolysed with mineral acids, with organic acids, such as citric and oxalic, or with carbon dioxide under pressure. Sucrose is fermented only after inversion; brewers' yeast brings about this inversion by means of the invertase which it contains, and ferments the invert sugar formed.

Maltose (Malt Sugar)

Maltose is formed, together with dextrin, by the hydrolysis of starch with acids, or with the enzyme diastase. It reduces alkaline cupric solutions (Fehling's, but not Barfoed's). Maltose is characterised by its high specific rotation, which often reveals its presence in sugars as a constituent of added starch sugars.

Lactose (Milk Sugar)

Lactose is a white crystalline powder obtained from the whey of milk; it has not been found in the vegetable kingdom. It reduces Fehling's solution, and is hydrolysed by mineral acids.

POLYSACCHARIDES

Dextrin

The dextrins are polysaccharides of less complexity than starch, from which they are formed by heating, or, together with maltose, by hydrolysis; they are referred to under the collective name of dextrin. It is soluble in water but insoluble in alcohol, and gives a violet to red coloration with iodine. It is characteristic of starch syrup or fermented liquors derived from starch, and its presence in natural products arises from the addition of starch products.

Starch, Starch Syrup, and Starch Sugar

Starch is a naturally occurring polysaccharide complex, of high optical activity, but without reducing power. Solutions of starch in the cold give a characteristic blue colour reaction with iodine, which is discharged on heating but returns on cooling.

The first products of the hydrolysis of starch with diastase or with acids are maltose, 80 per cent., and dextrin, 20 per cent.; continued hydrolysis with acids for three to four hours converts the maltose and dextrin into glucose.

These reactions are employed commercially for the manufacture of starch syrup and starch sugar. The starch is heated at one to two atmospheres steam pressure with about twice its weight of dilute acid (about 0.2 per cent. strength), sulphuric, hydrochloric, or hydrofluoric acids being employed. The excess acid is removed with chalk (with sodium carbonate in the case of hydrochloric acid), and when sulphuric acid has been used, calcium sulphate remaining in solution passes into the product. The products contain glucose, maltose, and dextrin in amounts which vary considerably according to the method and degree of hydrolysis or so-called conversion; the opacity and reducing power vary widely. The lower converted products are colourless syrups containing large quantities of dextrin and maltose. The highly converted products, obtained by a longer hydrolysis, contain less dextrin and maltose, and more glucose, and consist of finely crystallised glucose ad-

mixed with syrup from which it is difficult to separate ; some varieties of starch sugar consist almost entirely of glucose. The products contain 2 to 8 per cent. of non-saccharic matter, and 0.4 to 0.6 per cent. of ash ; calcium sulphate, arsenic, and lead derived from sulphuric acid may be present.

Starch syrup finds many uses on account of its non-crystallisable nature, such as in the preparation of confectionery, jams, syrups, jellies, and for addition to honey. It may be used in baking, and as a malt substitute in brewing. It is only two-thirds as sweet as sucrose, however, and imparts a slight bitter taste by which it may sometimes be detected.

SOME QUALITATIVE TESTS FOR THE SUGARS OCCURRING IN FOODS

Solutions :

Fehling's Solution (see page 205).—Fehling's solution, on boiling with reducing sugars, *i.e.* glucose, fructose, lactose, or maltose, gives a reddish-yellow precipitate of cuprous oxide.

Barfoed's Solution.—14 gm. of crystallised copper acetate and 5 cc. of acetic acid are dissolved in 200 cc. of water. This reagent is reduced by glucose and fructose, but not by maltose or lactose.

Nylander's Alkaline Bismuth Solution.—2 gm. bismuth oxynitrate, 4 gm. of potassium sodium tartrate (Rochelle salt), and 8 gm. of sodium hydroxide are dissolved in 100 cc. of water ; after standing some time the solution is filtered. On boiling, a dark precipitate of metallic bismuth is obtained with glucose, fructose, or maltose, but not with lactose, whereby the latter can be distinguished from maltose when indicated by Fehling's and Barfoed's solutions.

Reagent.	Reaction.	Indication.
Concentrated sulphuric acid on solid or strong solution.	Charring.	Sucrose. Slight coloration with maltose.
Five per cent. caustic soda solution, boiling.	Browning.	Reducing sugars.
Fehling's solution. boiling.	Precipitate of cuprous oxide.	Glucose, fructose, lactose, or maltose.
(a) With sample.		
(b) With sample after boiling with dilute acid.	Precipitate of cuprous oxide.	If no precipitate in (a), sucrose or dextrin.
(c) With filtrate from Barfoed's solution made alkaline with ammonia.	Precipitate of cuprous oxide.	Maltose or lactose.
Barfoed's solution, boiling.	Precipitate of cuprous oxide.	Glucose or fructose.
Nylander's solution.	Precipitate of metallic bismuth.	Glucose, fructose, or maltose.
To cold sugar solution, slight excess of phenylhydrazine in an equal volume of acetic acid is added.	Yellow crystalline precipitate.	Insoluble in hot water, glucose, or fructose. Soluble in hot water, maltose, lactose, or dextrin.
A large excess of strong alcohol is added.	Gummy precipitate on standing.	Dextrin.
The solution is warmed on a steam bath with 70 per cent. nitric acid, concentrated, and cooled.	Crystals of mucic acid.	Lactose.
Diphenylamine (page 152).	Blue coloration.	Sucrose.

GENERAL METHODS OF EXAMINATION OF SUGARS

Concentration of Sugar Solutions

The specific gravities of aqueous solutions of sugars at 15.5° C. exceed that of water by amounts which are proportional to the percentage of sugars in the solution. This proportion is represented by the average multiple, 3.86. Thus a sugar

solution having a specific gravity of 1044 compared with water=1000, gives an excess gravity of $1044-1000=44$. This figure divided by 3.86 equals the grammes of sugar in 100 cc.

$$\text{of solution} = \frac{44}{3.86} = 11.4 \text{ gm.}$$

This affords a simple method of estimating the amount of sugar in solution when only negligible quantities of foreign matter are present.

Preparation and Clarification of Solutions

Preparation of the Sugar Solution

A 10 per cent. solution is usually employed ; this is obtained by direct weighing, or by dilution of a given solution, the concentration of which has been determined from its specific gravity. Confectionery, preserves, etc., are macerated with water, and the solution is filtered ; the residue is washed, and the total filtrate is made to a definite volume.

Clarification of the Solution

Suspended, colouring, and other impurities in sugar solutions obstruct the passage of the polarised beam or decrease the accuracy of the optical rotation reading, and may also affect the reducing power determination ; they must, therefore, be removed. Many reagents are used as clarifiers, including lead acetate, alumina cream, sodium aluminate, copper salts, mercuric nitrate, mineral acids, and animal charcoal ; some cases require special reagents. Of the above, alumina cream is perhaps the most satisfactory, but its clarifying powers are limited. Basic lead acetate is more efficient, but it precipitates fructose when the latter is present in large quantities, and the excess of lead, if not removed, may influence the opticity of the solution ; these considerations restrict its use. Normal lead acetate is a powerful and useful clarifier, and has no influence on fructose in solution ; it is not as efficient as the basic salt. The tendency of animal charcoal to absorb sugars renders its use unsuitable. It is sometimes useful, however, in extreme cases, but it must be previously digested with boiling dilute hydrochloric acid, and washed to remove the impurities.

Clarifiers are used in solution, in suspension, or in the solid form; the last method is much to be preferred, as it obviates the correction for the volume of the precipitate, and avoids addition of unnecessary excess of the reagent. For this purpose, finely powdered normal or basic lead acetate will meet the requirements of ordinary analysis. To a volume of the sugar solution very small quantities of the powder are added, with thorough shaking, and allowing to stand for five or ten minutes after each addition. Complete clarification is judged by the appearance of the solution, and by filtration of a test portion through a dry filter, when the solution should be perfectly clear and colourless. The whole solution is then filtered through a dry filter. The excess of lead is removed by the addition of solid sodium carbonate or sodium sulphate; this is delicately controlled by adding successive minute portions of the solid until the removal of the last trace of lead from the solution is indicated by the absence of turbidity at the point where the solid enters.

Alumina cream is prepared from a solution of aluminium sulphate made alkaline with excess of ammonia; the aluminium hydroxide is filtered, washed, and suspended in ten times its weight of water, or is dried at 60° C. and used as a solid.

Optical Rotation

The solution to be examined is made neutral before adjusting concentration (about 10 per cent.).

The instruments of various design in use for the measurement of optical activity may be generalised in the following description of the Laurent polarimeter, which embodies all essentials, and is eminently suitable for public health analysis (Fig. 47).

The beam of monochromatic light is supplied by sodium chloride suspended in platinum baskets A, over the bunsen flame from T placed 20 cm. distant. The ray is polarised by the polariser contained in the barrel R, and is filtered if necessary from blue light by passing through a crystal of potassium dichromate, which may be removed in the case of dark solutions. A half-moon quartz wedge at P rotates half of the beam through 90°; thus the planes of polarisation of the right

and left half of the field are at right angles to each other. The beam then traverses the length of the sugar solution contained in a tube placed in the body of the instrument L. It then passes through the analyser below F, and through the eyepiece O. The plane of polarisation is determined with the analyser by means of some arbitrary relationship, provided in the case of the Laurent instrument by the quartz wedge. This, as described above, divides the field into halves, polarised at right angles to each other. Thus when one half coincides with the plane of the analyser it passes through completely; the other half, being at right angles, is at the same time cut off: the

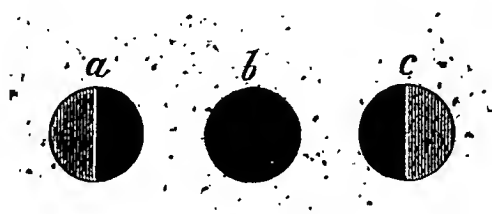


Fig. 48.

first half presents a bright field, the second half a dark field (c, Fig. 48). On rotating the analyser, the two halves of the field pass from dark to light, but in the opposite order to each other; when one is dark the other is light, and *vice versa*. The midway point, where both halves are equally illuminated (b, Fig. 48), is taken as the arbitrary position of the analyser to the plane of polarisation. The analyser is adjusted to this position before and after the insertion of the solution tube, and the extra rotation of the analyser to reproduce the point of equiluminosity, gives the angle through which the plane of polarisation has been rotated. This is noted as being to the right or the left, according to which the rotation is dextro or laevo, positive or negative respectively. The reading can be made on two scales C, one a protractor which gives the rotation in angular degrees, and one, used only with a standard solution of cane sugar, which gives percentage of sucrose.

The instrument is used with the lever X raised by U, and when necessary the luminosity of the field is increased by lowering this lever.

The temperature of the solution during observation must be known. It is considered sufficient to note the temperature of the solution immediately before use if it be at room temperature, but very accurate results are obtained only by controlling the temperature, especially if fructose be present. This is effected, and the temperature of the solution is brought to any desired point, by the use of a jacketed tube (Fig. 49) through which circulates a continuous stream of water from a constant temperature bath or thermostat. 20° C. is the standard temperature for specific rotation and polarimetric determinations.

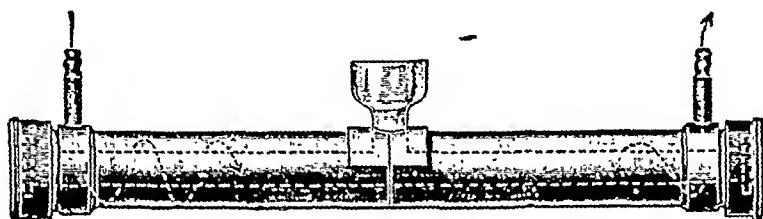


Fig. 49.

PROCESS :

If mutarotation be present, as indicated by a gradual change in rotation during observation, it is removed in a fresh portion of the sample, by making slightly alkaline with a few drops of liquor ammonia and heating to boiling ; the solution is cooled, neutralised, and made to a definite volume of suitable concentration (about 10 per cent.), and clarified. The polarimeter tubes, which are supplied in various lengths, of which the 2 dm. tube is most suitable for general use, is filled in a vertical position ; the glass disc is then slipped on from the side, avoiding air bubbles, and is retained in position by the flange.

The determination is carried out in a dark room. The instrument is first adjusted to zero, the field is focused by the eyepiece O, and the screw F is turned until equiluminosity of the field is obtained ; this screw remains unaltered in position during the examination. The tube, filled with sugar solution, is now placed in L and the field is focused anew. According as the shadow is to the right or left, so the sugar is dextro- or laevo-rotary, and the analyser must be turned in that direction by the screw G until equiluminosity is restored. The reading is taken between the zero on the scale and the zero on the

vernier; the mean of several readings should be taken. In the Laurent instrument, the divisions on the respective verniers equal $\frac{1}{10}$ those on the percentage scale, and 2 minutes on the degree scale. Each division on the degree scale represents $0.5^\circ = 30$ minutes. The minutes are calculated to decimal parts of a degree.

SPECIFIC ROTATION, 20° C. , 10 PER CENT. SOLUTION

Sugar.	$[\alpha]_D$.
Glucose	$+52.7^\circ$
Fructose	-93.7°
Invert sugar	-20.7°
Sucrose	$+66.6^\circ$
Lactose (Aq.)	$+52.5^\circ$
Lactose, Anhydrous	$+55.3^\circ$
Maltose	$+138.0^\circ$
Dextrin	$+200^\circ$ (average)
Starch Syrup	$+115^\circ$ (average)

CALCULATION OF RESULTS

From the angular rotation observed of a solution of a known sugar, and the specific rotation of the sugar, the gm. of sugar in 1 cc. of the solution is calculated from the following formula:—

$$p = \frac{R}{l \times [\alpha]_D}$$

when p = gm. of sugar in 1 cc. of solution,

R = rotation observed at 20° C. ,

$[\alpha]_D$ = specific rotation,

l = length of solution in decims.

EXAMPLE:

2 dem. of a solution of lactose, prepared by clarifying a sample of milk without change of volume, gave an angular rotation of 4 degrees 32 minutes at 20° C.

32 minutes = $\frac{32}{60} \times \frac{100}{1} = 0.533$ degree; therefore reading = 4.533 degrees.

Therefore gm. anhydrous lactose in 1 cc. = $\frac{R}{l \times [\alpha]_D}$

$$= \frac{4.533}{2 \times 55.3}$$

0.041 gm. in 1 cc. = 4.1 per cent.

Copper-reducing Power

The copper-reducing power of a sugar is measured by the amount of cuprous oxide formed, from an alkaline cupric oxide solution, by a standard weight of the sugar. The precipitated cuprous oxide may be collected, and weighed as cuprous oxide or as copper; or the determination may be made volumetrically, in which case the copper-reducing power is measured as the amount of sugar required to reduce completely a given amount of cupric salt.

Solutions required: Fehling's solution.

(a) 34.64 gm. crystallised copper sulphate is dissolved in water, and made to 500 cc.

(b) 173 gm. of pure Rochelle salt and 65 gm. of sodium hydroxide are dissolved in water, and made to 500 cc.

The two solutions are stored separately, and for use are mixed in equal proportions, *i.e.* 5 cc. of each of the above solutions give 10 cc. of Fehling's solution.

GRAVIMETRIC ESTIMATION

Slight auto-reduction takes place on heating the mixed solution alone. This auto-reduction depends largely on the impurities of the reagents employed in the preparation of the Fehling's solution, and if commercial Rochelle salt is used, it may be considerable. In any case, a certain amount of auto-reduction takes place, and each determination of reducing power is accompanied by a parallel control estimation on the Fehling's solution alone, and the auto-reduction is deducted. The auto-reduction of Fehling's solution increases with its age, and when found to be high it is advisable to make a fresh solution. Contamination of the solution with organic matter, such as filter paper, is avoided. Small variations in the composition of the solution may have appreciable effects on the values it gives, and strict accuracy in its preparation is necessary.

The relationship between the cuprous oxide precipitated, and the weight of the sugar added, is influenced by the concentration of the sugar in solution, by the time of heating, and

other conditions. Therefore, in order to ensure concordant results, it becomes necessary to employ standard conditions; the following method is standard for general application.

Process (Brown, Morris, and Millar):

25 cc. of each solution are mixed and diluted to 100 cc. less the volume of the sugar solution to be added. The mixture is heated in a small beaker on a water bath, and when the

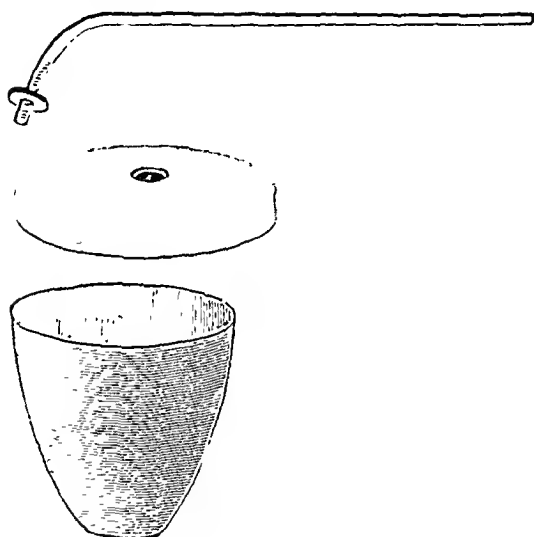


Fig. 50.

temperature has reached that of the bath, the weighed or measured sugar solution is added; the amount of added sugar is arranged such as to precipitate about 0.2 gm. (within 0.15 to 0.35 gm.) of cuprous oxide. The beaker is covered with a clock glass, and the heating continued for exactly twelve minutes. The precipitated cuprous oxide is at once rapidly filtered hot

through a Gooch crucible, and is washed with hot distilled water, alcohol, and finally ether, and dried in a steam oven. The asbestos used in the Gooch crucible is previously purified, as already described, otherwise soluble mineral matter may be extracted by the Fehling's solution and a loss experienced. Several methods of dealing with the cuprous oxide are practised, including oxidation to cupric oxide; the most convenient and a very accurate method is to reduce the cuprous oxide to metallic copper by heating, with a small flame, in a Rose crucible (Fig. 50) attached to a hydrogen supply.

In the case of oxidation this is best carried out by heating the Gooch crucible placed in a porcelain crucible (never directly) over a good Bunsen flame (not a blowpipe); the gentle and uniform heating of the Gooch crucible, which is essential for accuracy, is thus assured. The heating is con-

tinued until oxidation is complete, as shown by the Gooch crucible and contents remaining constant in weight.

Each estimation is accompanied by a control on the Fehling's solution itself, under identical conditions, and the auto-reduction is deducted.

The weight of copper or copper oxide is now referred to the following table,¹ which gives the values of reducing sugar to which the weight corresponds:—

Sugar Mgms.	GLUCOSE.			FRUCTOSE.			INVERT SUGAR.		
	Cu Gms.	CuO Gms	CuO corre- sponding to 1 Gm.	Cu Gms.	CuO Gms.	CuO corre- sponding to 1 Gm.	Cu Gms.	CuO Gms.	CuO corre- sponding to 1 Gm.
50	0.1030	0.1289	2.578	0.0923	0.1155	2.310	0.0975	0.1221	2.442
55	0.1134	0.1422	2.585	0.1027	0.1287	2.341	0.1076	0.1349	2.453
60	0.1238	0.1552	2.587	0.1122	0.1407	2.345	0.1176	0.1474	2.457
65	0.1342	0.1682	2.589	0.1216	0.1524	2.346	0.1275	0.1598	2.459
70	0.1443	0.1809	2.585	0.1312	0.1645	2.350	0.1373	0.1721	2.459
75	0.1543	0.1935	2.580	0.1405	0.1761	2.349	0.1468	0.1840	2.454
80	0.1644	0.2061	2.577	0.1500	0.1881	2.351	0.1566	0.1963	2.454
85	0.1740	0.2187	2.572	0.1590	0.1993	2.345	0.1662	0.2084	2.451
90	0.1834	0.2299	2.555	0.1686	0.2114	2.349	0.1755	0.2200	2.445
95	0.1930	0.2420	2.547	0.1774	0.2224	2.341	0.1848	0.2317	2.439
100	0.2027	0.2538	2.538	0.1862	0.2331	2.331	0.1941	0.2430	2.430
105	0.2123	0.2662	2.535	0.1952	0.2447	2.331	0.2034	0.2550	2.429
110	0.2218	0.2781	2.528	0.2040	0.2558	2.325	0.2128	0.2668	2.425
115	0.2313	0.2900	2.522	0.2129	0.2669	2.321	0.2220	0.2783	2.420
120	0.2404	0.3014	2.512	0.2215	0.2777	2.314	0.2311	0.2898	2.415
125	0.2496	0.3130	2.504	0.2303	0.2887	2.310	0.2400	0.3009	2.407
130	0.2585	0.3241	2.493	0.2390	0.2997	2.305	0.2489	0.3121	2.400
135	0.2675	0.3354	2.484	0.2477	0.3106	2.300	0.2578	0.3232	2.394
140	0.2762	0.3463	2.473	0.2559	0.3209	2.292	0.2663	0.3339	2.385
145	0.2850	0.3573	2.464	0.2641	0.3311	2.284	0.2750	0.3448	2.378
150	0.2934	0.3673	2.448	0.2723	0.3409	2.273	0.2832	0.3546	2.364
155	0.3020	0.3787	2.443	0.2805	0.3517	2.269	0.2915	0.3655	2.358
160	0.3103	0.3891	2.432	0.2889	0.3622	2.264	0.3002	0.3764	2.352
165	0.3187	0.3996	2.422	0.2972	0.3726	2.258	0.3086	0.3869	2.345
170	0.3268	0.4098	2.410	0.3053	0.3828	2.252	0.3167	0.3971	2.336
175	0.3350	0.4200	2.400	0.3134	0.3930	2.245	0.3251	0.4076	2.329
180	0.3431	0.4302	2.390	0.3216	0.4032	2.240	0.3331	0.4177	2.320
185	0.3508	0.4399	2.377	0.3297	0.4134	2.234	0.3410	0.4276	2.311
190	0.3590	0.4501	2.369	0.3377	0.4234	2.228	0.3490	0.4376	2.303
195	0.3668	0.4599	2.358	0.3457	0.4335	2.223	0.3570	0.4476	2.295
200	0.3745	0.4689	2.344	0.3539	0.4431	2.216	0.3650	0.4570	2.285
205	0.3822	0.4792	2.338	0.3616	0.4534	2.211	0.3726	0.4672	2.279

¹ Brown, Morris, and Millar, *Journal of the Chemical Society*, vol. lxxi. p. 281.

VOLUMETRIC ESTIMATION

The volumetric estimation of the reducing power is made by adding a solution of the sugar to a hot alkaline solution of cupric oxide, until this has been completely converted into cuprous oxide. With Fehling's solution this point is determined by testing, on a white tile, a drop of the clear solution extracted on a glass rod, with a drop of potassium ferrocyanide, or with Ling and Rendle's indicator.¹

10 cc. of Fehling's solution, in a large porcelain basin, is diluted with water and kept gently boiling. The addition of the sugar solution is continued until the cupric reaction is no longer given; a brown or red coloration is given with the smallest excess of cupric salt. Errors may arise through some oxidation of the cuprous oxide by contact with air, and it is necessary to carry out the titration as rapidly as possible; several minutes are required, and, speaking generally, the method gives slightly high results.

In view of the empirical relationship between Fehling's solution and the reducing power of the sugars, and also the variable auto-reduction of the solution, it is advisable to standardise it against a standard solution of pure glucose or inverted cane sugar.

1 cc. of Fehling's solution equals

5.0 mgm. of glucose, fructose, or invert sugar.

4.75 mgm. of cane sugar after inversion.

6.78 mgm. of lactose.

8.07 mgm. of maltose.

Pavy-Fehling Solution

The difficulties attached to the use of an indicator are avoided by the use of ammonia, which holds the cuprous oxide in solution, and at the same time intensifies the blue colour of the solution, thus enabling the end point, at which the colour is discharged, to be determined with accuracy. This is the

¹ 1 gm. of ferrous ammonium sulphate and 1 gm. of ammonium thiocyanate are dissolved in 10 cc. of water with gentle warming. The solution is decolorised before use, by shaking with a trace of zinc dust, and is filtered; it should be freshly prepared for use.

principle of the Pavy-Fehling solution, which is a dilute Fehling solution to which ammonia has been added.

Solution required :

The Pavy-Fehling solution may be prepared (1) by direct weighing of the reagents, or (2) by diluting Fehling solution.

(1) 4.1568 gm. of recrystallised copper sulphate is dissolved in 200 cc. of water ; 20.4 gm. of Rochelle salt and 20.4 gm. of potassium hydroxide are dissolved in another 200 cc. of

water, and the two solutions are mixed and cooled. 300 cc. of strong ammonia (sp. gr. 0.880) is added, and the whole is made to 1 litre.

(2) 120 cc. of Fehling solution, 300 cc. of liquor ammonia (sp. gr. 0.880), and 400 cc. of 12 per cent. sodium hydroxide solution are mixed and made to 1 litre with water.

One molecule of glucose reduces six molecules of cupric oxide in Pavy solution, instead of five in Fehling solution, and hence Pavy solution is *one-tenth* the value of Fehling solution, i.e. 1 cc. equals 0.5 mgm. of glucose.

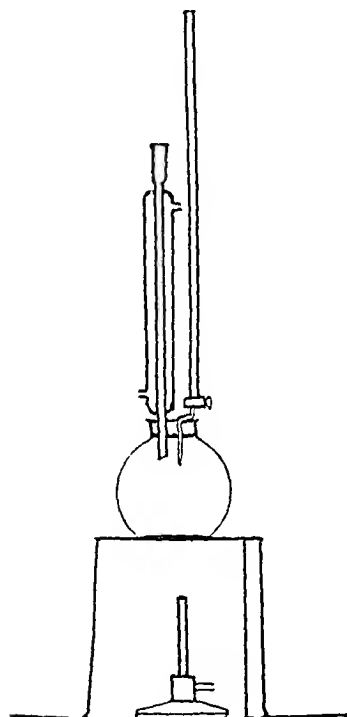


Fig. 51.

Process :

The titration flask, Fig. 51, of about 100 cc. capacity (small spherical weighing bottle), is closed with a two-holed rubber stopper, into one hole of which fits the long narrow tip of a burette ; the other hole carries a narrow tube fused to the end of a short condenser held in a clamp.

10 cc. of the Pavy-Fehling solution and 10 cc. of water are measured into the flask, and the burette is filled with the sugar solution to be examined, suitably diluted to a concentration of from 0.05 to 0.1 per cent. The whole is kept boiling and the sugar solution is added in small portions. The reduc-

tion of the Pavy-Fehling solution is not immediate, and about half a minute is required after each addition to obtain completion of the reaction. Meanwhile ammonia is escaping, and finally it may not be able to retain the cuprie and euprous oxides in solution, thus invalidating the titration; the condenser does not prevent the escape of the ammonia, but retards it sufficiently to give a longer available time for titration than otherwise. The deep blue colour passes to light green, and finally a colourless solution is obtained. There is a tendency to add an excess of sugar solution, and repetitions aiming at a minimum amount are necessary. If no appreciable excess has been added, the green colour returns on ceasing the boiling, owing to the entry of air into the flask on cooling; there is no danger of this occurring and introducing an error if the boiling is not interrupted during titration.

Preliminary titrations occasionally are required to ascertain and adjust the concentrations of sugar solutions of uncertain reducing power.

EXAMPLES :

Gravimetric.—50 cc. of Fehling's solution is diluted to 90 cc., and 10 cc. of a solution of invert sugar is added. The process is as described on page 206, and the cuprous oxide is converted into cupric oxide. CuO obtained = 0.2668 gm.; from table = 0.110 gm. inverted sugar.

Therefore solution contains 1.10 gm. invert sugar in 100 cc.

Volumetric.—10 cc. of Pavy-Fehling solution requires 12.3 cc. of a solution of glucose diluted to 1 in 10.

10 cc. of Pavy-Fehling solution = 0.005 gm. glucose.

Therefore diluted solution contains $\frac{0.005 \times 100}{12.3} = 0.04$ gm. glucose in 100 cc.

Therefore original solution contained 0.4 gm. glucose in 100 cc.

Inversion of Sucrose

Inversion of sucrose is effected with mineral or organic acids, or with invertase. Mineral acids are rapid in their action, but introduce errors by action on other convertible sugars which may be present, and for great accuracy the enzyme action is used.

PROCESSES :

(a) *With Hydrochloric Acid.*

To every 100 cc. of clarified sugar solution, containing not more than 20 gm. of sugar, is added 5 cc. of concentrated hydrochloric acid, and the mixture, in a flask containing a thermometer, is suspended, with occasional shaking, in a water bath exactly at 70° C. for fifteen minutes. Organic salts may neutralise some of the hydrochloric acid, and where large quantities of ash are present, as in molasses, 6 cc. of acid is taken. The solution is then rapidly cooled, exactly neutralised with sodium hydroxide, made to a definite volume, clarified if necessary, and filtered.

(b) *With Citric Acid*¹

The sugar solution, diluted to 5 per cent. strength or under, is made faintly acid with normal sulphuric acid, and 10 gm. of citric acid per 100 cc. is added. The mixture is boiled for ten minutes; complete hydrolysis of sucrose is effected, and maltose and lactose remain unchanged. The solution is cooled, and the process completed as in the foregoing.

(c) *With Invertase*

Yeast (which is rich in invertase) is pressed, and shaken with alcohol; after decanting the alcohol the solid residue is dried at 30 to 40° C.

About 1 gm. of yeast, freshly prepared as above, is macerated with 50 cc. of water, and the solution, after filtration, is added to 100 cc. of the clarified sugar solution of about 10 per cent. concentration; the solution must be neutral or slightly acid with acetic acid. The mixture, contained in a bottle closed with a cotton-wool plug, is placed in a water bath at 40° C. for four to five hours. Change in volume produces difficulties in comparison with the foregoing process. Variation in composition can be avoided by fitting a long glass tube, of approximate diameter as the neck of the flask. The mixture is finally heated for two minutes, to destroy the organic matter. The majority of food-processes are completed as in the two foregoing: sucrose, invert sugar, maltose, and also, in the case

¹ Davis and Daish, *Journal of Agriculture*

As the invertase itself may have appreciable opticity and reducing power, it must be treated alone in a control flask in the same manner as the sugar solution, and the opticity and reducing power of the invertase solution are deducted from those of the inverted sugar solution.

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THE QUANTITATIVE ANALYSIS OF SUGAR MIXTURES

THE public health analyst has to deal with sugar mixtures derived from the table-sugar industry, consisting of sucrose and invert sugars, with preserves and confectionery which may contain in addition starch syrup or starch sugar, and with milk and milk products characterised by the presence of lactose. Sucrose, artificial invert sugar, and starch sugar are widely used for admixture with natural products. Confectionery employs all the products of the sugar industries, together with large quantities of starch sugar.

The foodstuffs to be examined for sugars may be divided into the following classes:—

(1) Unadulterated table sugars, high-grade syrups and honey, consisting of sucrose and invert sugar.

(2) Low-grade syrups, treacles, molasses, jams, etc., containing sucrose, invert sugar, and disturbing organic matter.

(3) Sugar substances containing added starch syrup.

With pure products, class 1, accurate estimations of sucrose and invert sugar by opticity and Fehling's solution present no special difficulty. The same methods are applied to class 2, but the results are often appreciably affected by the influence on opticity and reducing power of the non-saccharic organic impurities which are difficult to remove. In the case of class 3, substances containing starch syrup, the presence of the syrup, by virtue of its complexity and considerable variation in composition, opticity, and reducing power, introduces difficulties in its estimation, which is therefore only approximate as the total syrup added.

The analysis of the sugars occurring in the majority of foodstuffs resolves into an estimation of sucrose, invert sugar, and added starch syrup or starch sugar, and also, in the case of milk products, of lactose.

Polarisation before Inversion

When the approximate composition of the sugar is known, the normal rotary power can be roughly gauged from the concentration; an abnormal dextro-rotation is probably due to maltose or dextrin, and suggests added starch syrup.

The proportionate and marked change in specific rotation of fructose with change of temperature provides a method for the estimation of invert sugar.

Thus where $R' - R'^1$ is the observed change in angular rotation of 1 dem. of the solution with change of temperature from t to t^1 ° C., and I is the weight in gm. of the invert sugar in 100 cc. of the solution at 20° C., then

$$I = \frac{R' - R'^1}{0.3095 (t - t^1)}$$

At 87.3° C. the opticity of invert sugar is zero, and any rotation observed is due to other sugars, usually sucrose and starch syrup; therefore rotation due to sugars other than sucrose and invert sugar,

$$= R \text{ at } 87.3^\circ \text{ C.} - \frac{66.6 \times S}{100}$$

where S is the sucrose (if present) in 100 cc. of solution.

If this is starch syrup, an approximate determination is calculated by using the average specific rotation +115 for starch syrup.

Polarisation after Inversion

In the presence of starch, maltose, lactose, or other convertible sugars, the sucrose is inverted by invertase or citric acid; in other cases with hydrochloric acid. The inverted solution is made to twice the original volume, and the polarisation readings obtained are multiplied by two to correspond with the original concentration. The product of inversion of mixtures of sucrose and invert sugar, of which the majority of sugar foods consist, is invert sugar which has a negative specific rotation of -20.7 at 20° C.; a positive rotation in these cases indicates the presence of added starch syrup or starch sugar.

Inversion is thus accompanied by a change in rotation which is proportional to the amount of sucrose in solution, since the

change in specific rotation from that of sucrose to that of invert sugar is definite.

Thus let S = gm. of sucrose in 100 cc., and
 D = angular deviation of 1 dm. after inversion.

$$\text{Then } S = \frac{100 \times D}{95.0 - \frac{t}{3}}, \text{ or, at } 20^{\circ} \text{ C., } S = \frac{100 \times D}{88.33}.$$

When the sugar mixture contains only sucrose and invert sugar, the latter can be calculated from the initial angular rotation after subtracting that due to the sucrose.

When S = gm. of sucrose in 100 cc. of the solution ; I = gm. of invert sugar in 100 cc., and R = the initial rotation of 1 dm. of the sugar solution, then at 20° C. $I = \frac{66.6 \times S - 100 \times R}{20.7}.$

Reducing Power

The reducing power before inversion gives the invert sugar, extra glucose, maltose, and, if present, lactose ; it is calculated as glucose from the table on page 207. The increase in reducing power after inversion is due to the invert sugar formed from sucrose ; 100 gm. of invert sugar equals 95 gm. of sucrose.

$$\text{Sucrose} = \frac{95 \times \text{invert sugar by increase of reducing power}}{100}.$$

Sucrose

An accurate value for sucrose is always given by inversion. In the presence of low-grade products such as molasses and of starch syrup, inversion is made with invertase or citric acid.

Invert Sugar

In the absence of other reducing sugars (starch syrup, etc.), invert sugar is most conveniently determined by Fehling's solution ; in the presence of starch syrup, by change in rotation with temperature.

Starch Syrup

There is no known reliable method for determining the amounts of extra glucose, maltose, and dextrin, derived from starch syrup, admixed with sucrose and invert sugar. It is

detected by the high optieity which it imparts to the mixture and by the presenee of dextrin and possibly caleium sulphate; it is estimated by the rotation at 87.3° C., or, in the case of treacle, by Jones' formula (page 220).

Dextrin ¹

To 100 cc. of a 10 per cent. solution of the sugar substance is added for each gramme of reducing sugar 0.5 gm. manganese dioxide, 2 cc. of 30 per cent. solution of sodium hydroxide, and 30 cc. of 30 per cent. hydrogen peroxide. The solution is boiled for one hour, cooled, neutralised with acetic acid, elarified, made to a definite volume, and polarised. The opticity. corrected for sucrose present, is caleulated to dextrin.

¹ F. Vollant, *Analyst*, 1911, p. 588.

SUGAR PRODUCTS

TABLE SUGAR

TABLE sugar is prepared from the extracted juice of the sugar cane, of the beet, and of the maple. The aqueous extract is clarified with lime, clay, etc., filtered and concentrated. The raw brown sugar which crystallises is further recrystallised and yields anhydrous crystals of high purity. The mother liquors contain sucrose and invert sugar, and are sold as treacle and syrup. Lower grades of sugar, according to the degree of separation from the invert sugar (called uncrystallisable sugar-slime), are obtained intermediate between the raw and refined sugar.

AVERAGE PERCENTAGE COMPOSITION OF PRODUCTS
OF THE CANE SUGAR INDUSTRY

	Sucrose.	Invert Sugar.	Water.	Ash.
Refined sugar .	96 to 99	1.2 to 0.2	1.0	0.5
White coffee sugar .	91.2	2.8	5.0	1.0
Yellow sugar . .	88.0	4.4	5.5	1.6
Raw sugar . . .	80.0	8.0	8.0	2.0
Treacle	45.0	21.3	21.2	7.6
Molasses . . .	36.4	20.0	30.0	8.2

Loaf and granulated sugar consists of almost pure sucrose; adulteration with other sugars is practically unknown, but colouring matter is sometimes added.

A complete analysis of table sugar includes the following determinations :—

- (1) Water.
- (2) Opticity before and after inversion : calculation of sucrose.

- (3) Reducing power before and after inversion : calculation of reducing sugars and of sucrose.
- (4) Matter insoluble in water.
- (5) Ash.

Water

10 gm. of powdered sugar, weighed in a weighing bottle, is dried at 60° C. for twelve hours.

Polarimeter Examination

For an angular reading polarimeter, 20 gm. in 100 cc. is a suitable concentration. The solution is clarified, if necessary, with the smallest amount of solid lead acetate, the excess of which is removed with sodium sulphate. The solution is filtered through a dry filter and polarised at 20° C. in a 2 dm. tube ; any mutarotation after ten minutes, or a reading showing over 100 per cent. sucrose, indicates added starch sugar. 50 cc. of the solution is then inverted with 5 cc. of concentrated hydrochloric acid at 70° C. for fifteen minutes, cooled, and made to 100 cc. ; the rotation is taken at 20° C. and multiplied by two to correspond with the original concentration. From the change in opticity with inversion the sucrose is calculated.

EXAMPLE :

2 dm. of a 20 per cent. sugar solution gave a polarisation of +25.8
 After inversion 2 dm. of the 10 per cent. solution gave -4.3
 Therefore 2 dm. of the original 20 per cent. solution would give -8.6
 That is, deviation of rotation for 2 dm. on inversion of +25.8 to -8.6 =
 34.4, and therefore the deviation for 1 dm. = 17.2.

From the formula given on page 215,

$$\text{Grammes of sucrose in 100 cc., } S = \frac{100D}{95.0 - \frac{t}{3}} = \frac{100 \times 17.2}{88.33} = 19.47$$

Therefore as 100 cc. of solution contains 20 gm. of the sample, sucrose
 in the sample = $\frac{19.47 \times 100}{20} = 97.35$ per cent.

Reducing Power

The initial reducing power of a good grade sugar is small, and in the absence of adulteration represents invert sugar.

Invert Sugar¹

25 gm. of the sample is dissolved in 100 cc. of water; 20 cc. of this solution, after clarification if necessary, is mixed with 20 cc. of Fehling's solution and warmed for ten minutes at 60 to 62° C. 60 cc. of cold water is then added, and the whole is filtered rapidly through a Gooch crucible. The cuprous oxide is oxidised (as described on page 206).

Invert sugar = $\text{CuO} \times 0.453$.

Insoluble Matter

100 gm. of the sugar is dissolved in water, and the insoluble matter is allowed to settle overnight. If the quantity is appreciable it is estimated by filtering through a weighed filter paper as for suspended solids in water. Any sediment may contain colouring matter. Crude additions, such as sand, chalk, starch, and insoluble mineral matter, are revealed at once in the insoluble matter, which in such cases must be examined further.

Ash

The incineration of sugar in the usual way is liable to troublesome frothing; this can be partially overcome by directing the bunsen flame, in the early stages of the heating, on to the surface of the char. Frothing can be best avoided, and decarbonisation hastened, by moistening the char with a few drops of sulphuric acid. In this way the ash is obtained as sulphates; ordinarily, carbonates predominate in the ash, but in any case the ash indicates only the bases in the sugar. The bases as sulphates more nearly represent the weight of original organic salts, and above 1 per cent. suggest added mineral matter.

TREACLE AND SYRUP

The by-products of the sugar industry contain sucrose and invert sugar. The higher-grade products are sold as syrup, treacle, and under fancy names. Some figures have already

¹ Pellet, *Bull. Ass. Chim. Sucr.*, 1913, 31, p. 182.

been given which show the composition of inferior grades of sugars; treacle and syrup are not very characteristic in their composition, but the following table gives general percentage figures :—

	Cane.	Beet.
Sucrose	35 to 50	50
Invert sugar	15 to 30	Trace
Non-saccharic organic matter .	5	5
Ash	3 to 8	11
Water	20 to 25	20

Beet syrups and treacles are distinguished from those of the cane by the practical absence of invert sugar. Adulteration with starch syrup is common, and water may be added. These products are examined by similar methods.

Water and Total Solids

10 gm. of the sample, weighed in a basin with a glass rod, is mixed with 10 gm. of freshly ignited quartz sand, and the whole is heated at 100° C. for twelve hours without removing the rod. The loss in weight represents water.

Sugars

These products, when unadulterated with starch syrup, are analysed by the methods described above. The presence of starch syrup may be declared by the manufacturers, and can be detected and estimated by the indications already mentioned. A quick method, giving an approximate figure for starch syrup, is by the use of Jones' formula¹ (which uses an average specific rotation of +109° for starch syrup and - 11° for inverted golden syrups and treacles). Percentage of added starch syrup = $\frac{100([\alpha]_D + 11)}{120}$ when $[\alpha]_D$ = specific rotation of sample after inversion, calculated on the total weight of sample (not on total solids present).

¹ *Analyst*, 1900, p. 87.

EXAMPLE :

A 20 per cent. solution of a treacle was prepared by dissolving 20 gm. of the sample in water and making to 100 cc.

50 cc. of this solution was inverted (page 211), neutralised, clarified, and made to 100 cc.

2 dm. of the inverted solution gave an angular rotation of 1.44° .

Specific rotation of sample $= \frac{1.44}{2 \times 0.1} = 7.20^\circ$.

Therefore added starch syrup $= \frac{100([\alpha]_D + 11)}{120} = \frac{100(7.2 + 11)}{120} = 15$ per cent.

HONEY

Honey consists normally of a mixture of glucose and fructose in approximately equal amounts, together with only a trace of sucrose. The amounts of glucose and fructose, however, may vary considerably, the fructose usually predominating; it is possible that some glucose may crystallise and be left in the comb. The following percentage figures are quoted from a number of analyses of English honey :—

Moisture	.	.	:	15.2 to 20.1
Glucose	.	.	.	42.0 to 20.6
Fructose	.	.	.	45.2 to 30.0
Sucrose	.	.	.	5.3 to 0.0
Total solids	.	.	.	84.9 to 74.9
Ash	.	.	.	0.15 to 0.4

In addition, honey contains traces of pollen, starch, wax, organic acids, and alkaloids. The variation in the normal constituents depends on the locality and the feeding of the bees. For instance, as much as 8 per cent. of sucrose has been found in the honey of bees working in the vicinity of sugar factories.

Adulteration of Honey

The adulteration of honey with table sugar, syrups, molasses, or starch syrup is detected by the general methods already described; starch syrup cannot be readily estimated. Artificial invert sugar cannot be distinguished from genuine honey by these means, as it closely approximates it in composition.

One artificial honey consists entirely of invert sugar obtained from the inversion of cane sugar with 0.1 per cent. of tartaric acid. Such artificial honeys, and to a certain extent the adulteration with invert sugar, etc., can be detected with the microscope by the absence of the pollen, fibre, etc., natural to genuine honey. Artificial honey is also characterised by a low ash and the absence of phosphates.

Moisture

The moisture is generally calculated by difference, but a direct estimation can be made as described in the analysis of treacle. Moisture above 25 per cent. can be assumed to have been artificially added.

Ash

10 gm. of the sample is slowly charred by surface heating and is then incinerated. A low ash suggests the addition of sucrose or invert sugar.

Total Solids

The ash obtained above is dissolved in 100 cc. of water and the specific gravity of the solution is taken. The excess gravity is deducted from the gravity of a 10 per cent. solution of the sample; the corrected gravity gives the sugars in solution by use of the divisor, 3.86.

Artificial Comb

Artificial honey, consisting of syrup or invert sugar, is sometimes filled into artificial combs, usually made of paraffin wax. When this is suspected, the comb is washed free from sugars and treated with concentrated sulphuric acid; a genuine comb chars, but paraffin remains unattacked.

JAMS

Table sugar is employed in the preparation of jams from fruit pulp or juice, and starch syrup or sugar is commonly used. The jam may thus contain sucrose, invert sugar, and

starch sugars, the estimation of which in admixture has been outlined in the foregoing pages. The adulterations to be expected in jams are foreign fibre and vegetable extract; apple pulp is of common occurrence. They are best discovered by a microscopic examination. As preservatives, boric and salicylic acid are frequently to be found.

Salicylic Acid

50 gm. of the sample is diluted with 50 cc. of water, and clarified with basic lead acetate; the whole is acidified with hydrochloric acid, filtered, and washed. The filtrate is extracted successively with ether, the ether is evaporated, and the extracted matter is dissolved in a little alcohol; this solution is transferred to a Nessler glass, made to the mark with water, and a few drops of iron alum solution are added. The coloration obtained is compared with colorations given with different amounts of a standard solution of salicylic acid, 1 cc. of which = 0.001 gm. of salicylic acid.

EXAMPLE :

50 gm. of jam treated as above described.

The extract coloration is matched by 4 cc. of the 0.1 per cent. salicylic acid solution, therefore the sample of jam contains in 100 gm.

$$\frac{100 \times 4 \times 0.001}{50} = 0.008 \text{ gm. of salicylic acid.}$$

$$= 0.008 \text{ per cent.}$$

CONFECTIONERY

Sweetmeats and confectionery are prepared from table sugar and invert sugar by a variety of processes of caramelisation and colouring in admixture with starch and other solids, starch syrup, starch sugar, treacle, molasses, and, in fact, almost every natural and artificial sweetening agent. Organic dyes are largely used, although colouring by means of skilful roasting has been made to produce a variety of shades. Mineral matter is often added as weighting, and alcoholic spirits are sometimes found.

An analysis is concerned with sugars, starches, colouring

matter, mineral matter, non-carbohydrates, sweeteners, and alcohol.

THE SUGARS IN MILK AND MILK PRODUCTS

Pure milk contains lactose and no other sugar. Condensed milk and other milk products (milk powders, milk chocolate, etc.) frequently contain added table and invert sugars or starch sugar.

The nature of milk and milk products renders their clarification, before polarimetric examination, difficult as errors are invariably introduced by the extreme means required. The clarifiers which have been recommended include copper sulphate, mercuric nitrate, picric, acetic, and citric acids. Of these, acid mercuric nitrate is very suitable for general use, giving a rapid and complete coagulation of the protein and fat, whereas basic lead acetate does not completely precipitate protein.

Lactose, by the Polarimeter, in the absence of other Sugars

In the case of milk products a 10 per cent. solution is made.

To about 100 gm. of sample in the case of milk (weighed exactly), or 100 cc. of diluted milk product, slight excess of acid mercuric nitrate solution (page 155) is added, and the mixture shaken. It is then filtered, under reduced pressure, through two filter papers in a Büchner funnel. The residue is washed with small quantities of water, and the total filtrate is made to 200 cc. The filtrate is filtered through a dry filter and examined in the polarimeter.

Multiplying the reading by two to allow for dilution, an example of the calculation is seen on page 204.

Sucrose

Sucrose present in milk products, such as condensed milk, is estimated by the change in opticity or reducing power after inversion. A 10 per cent. solution is shaken with 1 per cent. of finely ground citric acid, and after some minutes, the coagulated protein is filtered. The filtrate is examined optically,

and with Fehling's solution (lactose = $\text{CuO} \times 0.615$). It is then inverted, after the addition of a further 1 per cent. of citric acid, with ten minutes' boiling; the sucrose is inverted and the lactose remains unchanged. The sucrose, thus found by the change in rotation, together with the lactose estimated by the reducing power before inversion, account for the original rotation when other sugars are absent. If they require a total rotation appreciably greater than the original, invert sugar is also present; if less, starch sugar is probably present, and is confirmed by the presence of dextrin.

Saccharin in Sugars and Confectionery

Saccharin is intensely sweet, and imparts a distinct taste to a solution of one part in twenty thousand. It is reputed to be harmless, passing through the system unchanged. The detection of small quantities of saccharin is difficult. An acid solution of the sugar is extracted with ether, and the extract, after evaporation of the ether, is dissolved in water; if it contains saccharin it gives an intensely sweet taste. A portion of the extract is fused with a little sodium nitrate on a nickel lid, and the product is tested for sulphate with barium chloride; if saccharin be present the sulphate reaction is given. The purity of the reagents must be confirmed by a blank test.

PROPRIETARY FOODS

PROPRIETARY foods are generally advertised as being of benefit to infants and invalids. In these cases it is particularly important that their ingredients should be entirely harmless, readily digestible, and nutritious. They consist almost exclusively of starch, sugar, and milk products, with or without malt extract.

Moisture

10 gm. of finely divided material is dried at 100° C.

Cold-Water Extract and Residue

10 gm. of the dried substance is shaken with 100 cc. of water and allowed to stand for two hours and filtered; the filtrate is examined for sugars as below. The residue is washed with cold water, dried, and weighed; the loss represents the cold-water extract.

Lactose

To 25 cc. of the cold-water extract (without washings) is added 0.5 gm. of fresh pressed yeast; the flask is stoppered with a cotton-wool plug, and maintained at 25° C. for four days. At the completion of the fermentation, the mixture is heated to boiling for some minutes to destroy the activity of the yeast and to remove alcohol, filtered, clarified, and made to 50 cc. A parallel treatment is carried out on the same amount of yeast alone, and the optical rotation due to the yeast is deducted from that of the fermented solution. The corrected optical rotation of the final solution from the sample (representing a 5 per cent. solution of the original substance) is calculated to lactose.

Sucrose

20 cc. of the cold-water extract is examined in the polarimeter, before and after inversion with 10 per cent. citric acid.

Invert Sugar

The reducing power of 10 cc. of the cold-water extract is corrected for lactose and then calculated as invert sugar.

Soluble Phosphates

A portion of the aqueous extract is titrated with standard uranium acetate solution (page 177).

Fat

The dry residue from the cold-water extract is extracted, in a Soxhlet, with anhydrous ether, and the fat, after evaporation of the ether, and drying at 100° C., is weighed. Fat may be introduced with dried milk products.

Starch

The residue from the extraction of fat is boiled for three hours with 3 per cent. hydrochloric acid (20 cc. concentrated HCl with 200 cc. of water) under a reflux condenser, filtered through a weighed filter paper, and washed. The filtrate is neutralised, clarified, and made to a definite volume. By this means the starch is converted into glucose, which is estimated in the filtrate by Fehling's solution. $\text{Starch} = \text{glucose} \times 0.92$. Results by this method are somewhat low.

Fibre

The residue from the starch conversion is dried and weighed, as fibre.

Protein

The nitrogen, determined by Kjeldahl's method (page 174), is multiplied by 6.25.

Gluten

Gluten may be estimated in unbaked foods, by working between the fingers in a stream of water as for flour. Baking coagulates gluten.

Ash. Total Phosphates. Injurious Metals

The ash is obtained and weighed in the usual manner. It should be alkaline, and may be examined for mineral acid substances, as described for alcoholic liquors. The total phosphates is estimated by extracting the ash with dilute acetic acid, and titrating with standard uranium acetate solution. The ratio of soluble to total phosphates is an important factor in the nutriment value of phosphate foods, and it is questionable whether uncombined mineral phosphates (soluble phosphates) have any value in this respect. The ash from a separate portion of the sample is examined for injurious metals.

RICE

To improve the appearance of rice it is commonly polished with talc. Talc is the mineral steatite, magnesium silicate, and when the amount remaining with the grains is excessive, there is a presumption that it is prejudicial to health. It has been suggested that the permissible limit for mineral matter in rice should be 0.5 per cent.¹

Estimation of Talc ²

5 gm. of the sample, in a flask, is treated with 5 cc. of 3 per cent. hydrogen peroxide, 2 cc. of ammonia (strong ammonia, sp. gr. 0.880, diluted 1 in 3) and 3 cc. of water. To loosen the talc the whole is heated on a steam bath for some seconds, shaken intermittently for ten minutes, and the liquid with loose mineral matter is decanted into a small beaker; the residue is washed ten times by shaking with 10 cc. portions of water. To the total liquid 10 cc. of concentrated nitric acid is added, and boiled gently for ten minutes; the whole is filtered through an ashless filter paper, and the residue is ignited at a dull red heat and weighed.

¹ Dr. J. M. Hamill's *Report to the Local Government Board on 'facing' and other methods of preparing rice for sale* (1909).

² R. Kržižan, *Zeitschrift für Untersuchung der Nahrungs- und Genussmittel*, 1906, vol. xi. p. 641.

GENERAL METHODS OF ANALYSIS OF ALCOHOLIC LIQUORS

ALCOHOLIC liquors are those containing over 2 per cent. of proof spirit (*q.v.*), and are manufactured by the fermentation of starch or saccharic extracts. They include spirits, in which the alcohol is concentrated by distillation; wines from the juices of grapes; cider from apple, and perry from pear juice; beers from malt; and a variety of cordials purporting to be prepared from natural sources. They vary so widely in their composition that it is impossible to give average figures.

These liquors are subject to adulteration with water, and fortification with methylated spirit; the latter may introduce methyl alcohol. The dangerous nature of methyl alcohol has again been demonstrated by the numerous fatal cases in America due to the consumption of 'wood alcohol.' In some cases starch sugar or syrup is added to the natural vegetable extract, and may introduce mineral acidity or arsenic.

In the majority of cases only an estimation of the alcohol is required, but the following includes some of the general methods of detailed analysis.

ALCOHOL

Two methods are in use for this determination. The alcohol may be separated by distillation, and the amount determined from the specific gravity of the distillate, or its concentration may be deduced from the change of specific gravity after removal of the alcohol by boiling; the former method is employed where absolute accuracy is necessary, but the latter gives sufficiently reliable results for ordinary purposes.

By Distillation

In Fig. 52 is shown the apparatus used by the Inland Revenue and Custom House authorities, but any similar arrangement will suffice.

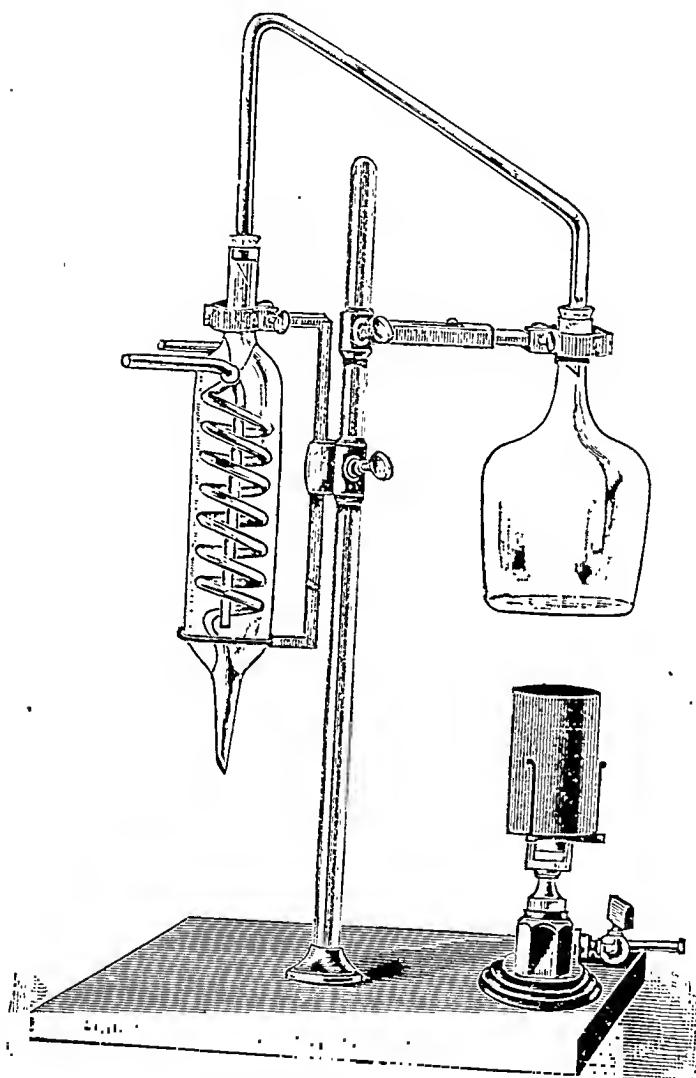


Fig. 52.

100 cc. of the sample is neutralised with sodium hydroxide solution, in the flask, and a few pieces of broken porcelain are added. With beer it is advisable previously to remove carbon dioxide by vigorous shaking. The distillate is collected in a 100 cc. graduated flask. In the case of beer, distillation is continued until the distillate measures about half the volume of beer originally taken: wines and spirits require to be distilled almost to dryness. The distillate is made to the original volume (100 cc.), giving a practically pure alcoholic solution of the same strength as the sample. The specific gravity of the distillate varies according to the amount of alcohol present. The specific gravity is therefore taken (with the Westphal balance), and by reference to the tables on pages 233-237, the amount of alcohol in the sample is found; it is important that the distillate be previously cooled to 15.5° C.

EXAMPLE :

Specific gravity of distillate at 15.5° C.=0.9885.

Therefore alcohol in sample, from tables=6.93 by weight, 8.63 by volume, per cent.

Indirect Method

The sample is very thoroughly shaken to remove carbon dioxide, and the specific gravity is taken. 100 cc. is boiled to about half bulk in the case of beer, and to about two-thirds in the case of wines and spirits; the liquid is cooled, made to the original volume (100 cc.), and the specific gravity of the alcohol-free liquid is taken. By calculation, and reference to tables, the amount of alcohol in the sample is obtained.

EXAMPLE :

Specific gravity of sample, original	=1.0150
Specific gravity of sample after removal of alcohol	=1.0265
Change in gravity due to removal of alcohol	=1.0265-1.0150=0.0115.
Therefore the gravity of the alcohol	=1.000-0.0115=0.9885.
From tables, alcohol=6.93 by weight, 8.63 by volume, per cent.	

ALCOHOL TABLE

Sp. Gr. at 15.5° C.	Per cent. of alcohol by weight.	Per cent. of alcohol by volume.	Sp. Gr. at 15.5° C.	Per cent. of alcohol by weight.	Per cent. of alcohol by volume.
1.0000	0.00	0.00	0.9790	13.92	17.17
0.9995	0.26	0.33	0.9785	14.36	17.70
0.9990	0.53	0.66	0.9780	14.82	18.25
0.9985	0.79	0.99	0.9775	15.25	18.78
0.9980	1.06	1.34	0.9770	15.67	19.28
0.9975	1.37	1.73	0.9765	16.08	19.78
0.9970	1.69	2.12	0.9760	16.46	20.24
0.9965	2.00	2.51	0.9755	16.85	20.71
0.9960	2.28	2.86	0.9750	17.25	21.19
0.9955	2.56	3.21	0.9745	17.67	21.69
0.9950	2.83	3.55	0.9740	18.08	22.18
0.9945	3.12	3.90	0.9735	18.46	22.64
0.9940	3.41	4.27	0.9730	18.85	23.10
0.9935	3.71	4.63	0.9725	19.25	23.58
0.9930	4.00	5.00	0.9720	19.67	24.08
0.9925	4.31	5.39	0.9715	20.08	24.58
0.9920	4.62	5.78	0.9710	20.50	25.07
0.9915	4.94	6.17	0.9705	20.92	25.57
0.9910	5.25	6.55	0.9700	21.31	26.04
0.9905	5.56	6.94	0.9695	21.69	26.49
0.9900	5.87	7.32	0.9690	22.08	26.95
0.9895	6.21	7.74	0.9685	22.46	27.40
0.9890	6.57	8.18	0.9680	22.85	27.86
0.9885	6.93	8.63	0.9675	23.23	28.31
0.9880	7.27	9.04	0.9670	23.62	28.77
0.9875	7.60	9.45	0.9665	24.00	29.22
0.9870	7.93	9.86	0.9660	24.38	29.67
0.9865	8.29	10.30	0.9655	24.77	30.13
0.9860	8.64	10.73	0.9650	25.14	30.57
0.9855	9.00	11.17	0.9645	25.50	30.98
0.9850	9.36	11.61	0.9640	25.86	31.40
0.9845	9.71	12.05	0.9635	26.20	31.80
0.9840	10.08	12.49	0.9630	26.53	32.19
0.9835	10.46	12.96	0.9625	26.87	32.58
0.9830	10.85	13.43	0.9620	27.21	32.98
0.9825	11.23	13.90	0.9615	27.57	33.39
0.9820	11.62	14.37	0.9610	27.93	33.81
0.9815	12.00	14.84	0.9605	28.25	34.18
0.9810	12.38	15.30	0.9600	28.56	34.54
0.9805	12.77	15.77	0.9595	28.87	34.90
0.9800	13.15	16.24	0.9590	29.20	35.28
0.9795	13.54	16.70	0.9585	29.53	35.66

Sp. Gr. at 15.5° C.	Per cent. of alcohol by weight.	Per cent. of alcohol by volume.	Sp. Gr. at 15.5° C.	Per cent. of alcohol by weight.	Per cent. of alcohol by volume.
0.9580	29.87	36.04	0.9365	41.55	49.02
0.9575	30.17	36.39	0.9360	41.80	49.29
0.9570	30.44	36.70	0.9355	42.05	49.55
0.9565	30.72	37.02	0.9350	42.29	49.81
0.9560	31.00	37.34	0.9345	42.52	50.06
0.9555	31.31	37.69	0.9340	42.76	50.31
0.9550	31.62	38.04	0.9335	43.00	50.57
0.9545	31.94	38.40	0.9330	43.24	50.82
0.9540	32.25	38.75	0.9325	43.48	51.07
0.9535	32.56	39.11	0.9320	43.71	51.32
0.9530	32.87	39.47	0.9315	43.95	51.58
0.9525	33.18	39.81	0.9310	44.18	51.82
0.9520	33.47	40.14	0.9305	44.41	52.06
0.9515	33.76	40.47	0.9300	44.64	52.29
0.9510	34.05	40.79	0.9295	44.86	52.53
0.9505	34.29	41.05	0.9290	45.09	52.77
0.9500	34.52	41.32	0.9285	45.32	53.01
0.9495	34.76	41.58	0.9280	45.55	53.24
0.9490	35.00	41.84	0.9275	45.77	53.48
0.9485	35.25	42.12	0.9270	46.00	53.72
0.9480	35.50	42.40	0.9265	46.23	53.95
0.9475	35.75	42.67	0.9260	46.46	54.19
0.9470	36.00	42.95	0.9255	46.68	54.43
0.9465	36.28	43.26	0.9250	46.91	54.66
0.9460	36.56	43.56	0.9245	47.14	54.90
0.9455	36.83	43.87	0.9240	47.36	55.13
0.9450	37.11	44.18	0.9235	47.59	55.37
0.9445	37.39	44.49	0.9230	47.82	55.60
0.9440	37.67	44.79	0.9225	48.05	55.83
0.9435	37.94	45.10	0.9220	48.27	56.07
0.9430	38.22	45.41	0.9215	48.50	56.30
0.9425	38.50	45.71	0.9210	48.73	56.54
0.9420	38.78	46.02	0.9205	48.96	56.77
0.9415	39.05	46.32	0.9200	49.16	56.98
0.9410	39.30	46.59	0.9195	49.39	57.20
0.9405	39.55	46.86	0.9190	49.64	57.45
0.9400	39.80	47.13	0.9185	49.86	57.69
0.9395	40.05	47.40	0.9180	50.09	57.92
0.9390	40.30	47.67	0.9175	50.30	58.14
0.9385	40.55	47.94	0.9170	50.52	58.36
0.9380	40.80	48.21	0.9165	50.74	58.58
0.9375	41.05	48.48	0.9160	50.96	58.80
0.9370	41.30	48.75	0.9155	51.17	59.01

Sp. Gr. at 15.5° C.	Per cent. of alcohol by weight.	Per cent. of alcohol by volume.	Sp. Gr. at 15.5° C.	Per cent. of alcohol by weight.	Per cent. of alcohol by volume.
0.9150	51.38	59.22	0.8935	60.88	68.52
0.9145	51.58	59.43	0.8930	61.08	68.72
0.9140	51.79	59.63	0.8925	61.29	68.91
0.9135	52.00	59.84	0.8920	61.50	69.11
0.9130	52.23	60.07	0.8915	61.71	69.30
0.9125	52.45	60.30	0.8910	61.92	69.50
0.9120	52.68	60.52	0.8905	62.14	69.71
0.9115	52.91	60.74	0.8900	62.36	69.92
0.9110	53.13	60.97	0.8895	62.59	70.14
0.9105	53.35	61.19	0.8890	62.82	70.35
0.9100	53.57	61.40	0.8885	63.04	70.57
0.9095	53.78	61.62	0.8880	63.26	70.77
0.9090	54.00	61.84	0.8875	63.48	70.97
0.9085	54.24	62.07	0.8870	63.70	71.17
0.9080	54.48	62.31	0.8865	63.91	71.38
0.9075	54.71	62.55	0.8860	64.13	71.58
0.9070	54.95	62.79	0.8855	64.35	71.78
0.9065	55.18	63.02	0.8850	64.57	71.98
0.9060	55.41	63.24	0.8845	64.78	72.18
0.9055	55.64	63.46	0.8840	65.00	72.38
0.9050	55.86	63.69	0.8835	65.21	72.58
0.9045	56.09	63.91	0.8830	65.42	72.77
0.9040	56.32	64.14	0.8825	65.63	72.96
0.9035	56.55	64.36	0.8820	65.83	73.15
0.9030	56.77	64.58	0.8815	66.04	73.34
0.9025	57.00	64.80	0.8810	66.26	73.54
0.9020	57.22	65.01	0.8805	66.48	73.73
0.9015	57.42	65.21	0.8800	66.70	73.93
0.9010	57.63	65.41	0.8795	66.91	74.13
0.9005	57.83	65.61	0.8790	67.13	74.33
0.9000	58.05	65.81	0.8785	67.33	74.52
0.8995	58.27	66.03	0.8780	67.54	74.70
0.8990	58.50	66.25	0.8775	67.75	74.89
0.8985	58.73	66.47	0.8770	67.96	75.08
0.8980	58.95	66.69	0.8765	68.17	75.27
0.8975	59.17	66.90	0.8760	68.38	75.45
0.8970	59.39	67.11	0.8755	68.58	75.64
0.8965	59.61	67.32	0.8750	68.79	75.83
0.8960	59.83	67.53	0.8745	69.00	76.01
0.8955	60.04	67.73	0.8740	69.21	76.20
0.8950	60.26	67.93	0.8735	69.42	76.39
0.8945	60.46	68.13	0.8730	69.63	76.57
0.8940	60.67	68.33	0.8725	69.83	76.76

Sp. Gr. at 15.5° C.	Per cent. of alcohol by weight.	Per cent. of alcohol by volume.	Sp. Gr. at 15.5° C.	Per cent. of alcohol by weight.	Per cent. of alcohol by volume.
0.8720	70.04	76.94	0.8505	79.12	84.77
0.8715	70.24	77.12	0.8500	79.32	84.93
0.8710	70.44	77.29	0.8495	79.52	85.10
0.8705	70.64	77.46	0.8490	79.72	85.26
0.8700	70.84	77.64	0.8485	79.92	85.42
0.8695	71.04	77.82	0.8480	80.13	85.59
0.8690	71.25	78.00	0.8475	80.33	85.77
0.8685	71.46	78.18	0.8470	80.54	85.94
0.8680	71.67	78.36	0.8465	80.75	86.11
0.8675	71.88	78.55	0.8460	80.96	86.28
0.8670	72.09	78.73	0.8455	81.16	86.45
0.8665	72.30	78.93	0.8450	81.36	86.61
0.8660	72.52	79.12	0.8445	81.56	86.77
0.8655	72.74	79.31	0.8440	81.76	86.93
0.8650	72.96	79.50	0.8435	81.96	87.09
0.8645	73.17	79.68	0.8430	82.15	87.24
0.8640	73.38	79.86	0.8425	82.35	87.40
0.8635	73.58	80.04	0.8420	82.54	87.55
0.8630	73.79	80.22	0.8415	82.73	87.70
0.8625	74.00	80.40	0.8410	82.92	87.85
0.8620	74.23	80.60	0.8405	83.12	88.00
0.8615	74.45	80.80	0.8400	83.31	88.16
0.8610	74.68	81.00	0.8395	83.50	88.31
0.8605	74.91	81.20	0.8390	83.69	88.46
0.8600	75.14	81.40	0.8385	83.88	88.61
0.8595	75.36	81.60	0.8380	84.08	88.76
0.8590	75.59	81.80	0.8375	84.28	88.92
0.8585	75.82	82.00	0.8370	84.48	89.08
0.8580	76.04	82.19	0.8365	84.68	89.24
0.8575	76.25	82.37	0.8360	84.88	89.39
0.8570	76.46	82.54	0.8355	85.08	89.55
0.8565	76.67	82.72	0.8350	85.27	89.70
0.8560	76.88	82.90	0.8345	85.46	89.84
0.8555	77.08	83.07	0.8340	85.65	89.99
0.8550	77.29	83.25	0.8335	85.85	90.14
0.8545	77.50	83.43	0.8330	86.04	90.29
0.8540	77.71	83.60	0.8325	86.23	90.43
0.8535	77.92	83.78	0.8320	86.42	90.58
0.8530	78.12	83.94	0.8315	86.62	90.73
0.8525	78.32	84.11	0.8310	86.81	90.88
0.8520	78.52	84.27	0.8305	87.00	91.02
0.8515	78.72	84.44	0.8300	87.19	91.17
0.8510	78.92	84.60	0.8295	87.38	91.31

Sp. Gr. at 15.5° C.	Per cent. of alcohol by weight.	Per cent. of alcohol by volume.	Sp. Gr. at 15.5° C.	Per cent. of alcohol by weight.	Per cent. of alcohol by volume.
0.8290	87.58	91.46	0.8110	94.28	96.32
0.8285	87.77	91.60	0.8105	94.45	96.43
0.8280	87.96	91.75	0.8100	94.62	96.55
0.8275	88.16	91.90	0.8095	94.80	96.67
0.8270	88.36	92.05	0.8090	94.97	96.78
0.8265	88.56	92.21	0.8085	95.14	96.90
0.8260	88.76	92.36	0.8080	95.32	97.02
0.8255	88.96	92.51	0.8075	95.50	97.15
0.8250	89.16	92.66	0.8070	95.68	97.27
0.8245	89.35	92.80	0.8065	95.86	97.39
0.8240	89.54	92.94	0.8060	96.03	97.51
0.8235	89.73	93.09	0.8055	96.20	97.62
0.8230	89.92	93.23	0.8050	96.37	97.73
0.8225	90.11	93.36	0.8045	96.53	97.83
0.8220	90.29	93.49	0.8040	96.70	97.94
0.8215	90.46	93.62	0.8035	96.87	98.05
0.8210	90.64	93.75	0.8030	97.03	98.16
0.8205	90.82	93.87	0.8025	97.20	98.27
0.8200	91.00	94.00	0.8020	97.37	98.37
0.8195	91.18	94.13	0.8015	97.53	98.48
0.8190	91.36	94.26	0.8010	97.70	98.59
0.8185	91.54	94.38	0.8005	97.87	98.69
0.8180	91.71	94.51	0.8000	98.03	98.80
0.8175	91.89	94.64	0.7995	98.19	98.89
0.8170	92.07	94.76	0.7990	98.34	98.98
0.8165	92.26	94.90	0.7985	98.50	99.07
0.8160	92.44	95.03	0.7980	98.66	99.16
0.8155	92.63	95.16	0.7975	98.81	99.26
0.8150	92.81	95.29	0.7970	98.97	99.35
0.8145	93.00	95.42	0.7965	99.13	99.45
0.8140	93.18	95.55	0.7960	99.29	99.55
0.8135	93.37	95.69	0.7955	99.45	99.65
0.8130	93.55	95.82	0.7950	99.61	99.75
0.8125	93.74	95.95	0.7945	99.78	99.86
0.8120	93.92	96.08	0.7940	99.94	99.96
0.8115	94.10	96.20	0.7938	100.00	100.00

PROOF SPIRIT

The content of alcohol is generally expressed in terms of proof spirit. This is a ridiculous scale, and causes needless complications, but it is the basis of trade calculations. Proof spirit at 15.5°C has a specific gravity of 0.9198, and contains 49.24 per cent. of alcohol by weight, 57.06 per cent. by volume. Degrees under proof (U.P.) of a mixture give the percentage of water over and above that in the proof spirit present, *e.g.* 15° U.P. means 85 per cent. proof spirit and 15 per cent. water. Degrees over proof (O.P.) give the excess proof spirit, over 100 per cent. proof spirit, which is equivalent to the alcohol present; thus 15° O.P. indicates that alcohol is present in 100 parts to make 115 parts of proof spirit.

EXAMPLES OF CALCULATIONS :

- (1) A sample of whisky is 27 degrees O.P.; how much alcohol is present?

27 degrees O.P. = alcohol equal to 127 per cent. proof spirit =

$$\frac{127}{100} \times 49.24 = 62.53 \text{ per cent. alcohol by weight.}$$

$$\frac{127}{100} \times 57.06 = 72.47 \text{ per cent. alcohol by volume.}$$

- (2) Similarly in a sample 63 degrees U.P.

63 degrees U.P. = alcohol equal to $100 - 63 = 37$ per cent. proof spirit =

$$\frac{37}{100} \times 49.24 = 18.22 \text{ per cent. alcohol by weight.}$$

$$\frac{37}{100} \times 57.06 = 21.11 \text{ per cent. alcohol by volume.}$$

- (3) A sample of brandy contains 68.26 per cent. of alcohol by volume; express in terms of proof spirit.

Proof spirit contains 57.06 alcohol by volume, therefore alcohol in sample

$$\text{is equal to } \frac{68.26}{57.06} \times 100 = 120 \text{ per cent. proof spirit.}$$

$$120 - 100 = 20 \text{ degrees over proof.}$$

- (4) A sample contains 36.42 per cent. of alcohol by weight; express in terms of proof spirit.

Proof spirit contains 49.24 per cent. of alcohol by weight, therefore alcohol

$$\text{in sample} = \frac{36.42}{49.24} \times 100 = 74 \text{ per cent. proof spirit.}$$

$$= 100 - 74 = 26 \text{ degrees under proof.}$$

TOTAL SOLIDS

The total solids or extract is obtained by evaporating a measured amount of the liquor to dryness on a steam bath in the usual manner. It can be more conveniently determined from the gravity of the liquor after removing alcohol and other volatile matter by boiling, and making to the original volume ; the excess gravity (water=1000), divided by the divisor 4, gives the gm. of solids in 100 cc.

EXAMPLE :

100 cc. of beer, boiled to half bulk, cooled and made to 100 cc. gives a gravity of 1026.5 (water=1000).

Therefore solids in 100 cc. liquid = $\frac{1026.5 - 1000}{4} = \frac{26.5}{4} = 6.62$.

SUGARS

The sugars in solution, if any, are examined by the methods described in the foregoing. Wines and spirits contain naturally little or no sugar, but beer may contain appreciable quantities of dextrin and maltose.

ASH

The ash is obtained by ignition ; it is naturally alkaline.

MINERAL ACIDS

Mineral acids are absent from natural liquors, and their presence indicates adulteration.

Ashby's Test

A strip of porous tile is dipped at one end into a freshly prepared logwood solution, and air-dried ; a drop of the sample is added to only part of the logwood stain, and also allowed to air-dry. The presence of free mineral acids is shown by a red stain.

Estimation, Hehner's Method

The ash of a pure vegetable liquor is alkaline in consequence of the formation of carbonates from the organic matter, and the ash is only neutral when free mineral acid is present in the liquor. A quantitative estimation of free mineral acid is based

on these facts. To 25 cc. of the sample is added 25 cc. of N/10 sodium hydroxide. Any free mineral acid irretrievably neutralises an equivalent amount of the alkali; the alkali neutralised by organic acids becomes converted into an equivalent amount of alkaline carbonate on ignition. The mixture is evaporated to dryness, and ignited at a low temperature. A few drops of neutral hydrogen peroxide solution and 50 cc. of N/10 sulphuric acid is added; the mixture is warmed, and filtered, the filter being washed with boiling water. The filtrate plus washings is titrated with N/10 NaOH.

The alkali originally added above, in the absence of 'free' mineral acids, is returned at its full alkaline value, and neutralises 25 cc. of the 50 cc. N/10 sulphuric acid, leaving 25 cc. free. Any consumption of N/10 NaOH beyond 25 cc. in the final titration indicates free mineral acidity in the sample; each cc. of N/10 alkali above 25 cc. equals 0.0049 gm. free mineral acidity calculated as sulphuric acid.

Sulphurous Acid

Sulphurous acid is often used as a bleacher and clarifier of liquors. It is best detected, and estimated, by distilling the liquor with phosphoric acid; sulphur dioxide passes over in the distillate, and is estimated by titration with N/10 iodine solution (12.692 gm. iodine, with about 20 gm. potassium iodide per litre), using starch solution as indicator.

A delicate means of detecting sulphurous acid is to warm the solution, slightly acidified with hydrochloric acid, with zinc dust; sulphuretted hydrogen is liberated, and gives the characteristic stain on lead acetate paper.

ORGANIC ACIDS AND SALTS

The organic acids in vegetable liquors are separated by distillation into volatile acids and non-volatile acids. The liquor is distilled to two-thirds its volume, and the distillate and residue are separately titrated with N/10 sodium hydroxide, using phenolphthalein indicator; volatile acidity is calculated as acetic acid.

The residue may contain lactic, tartaric, or citric acids.

With beers it is usual to calculate the residual acidity as lactic acid, and in the case of wines as tartaric acid (in the absence of mineral acidity).

SPIRITS

Spirits are obtained from fermented liquors by distillation. They are characterised by the presence of a high percentage of alcohol, by higher alcohols, and by esters. Adulteration of spirits includes addition of methylated spirits, and a variety of flavourings and colourings; many spirits are indeed entirely artificial, consisting of flavoured and coloured solutions of alcohol. These latter are low in the by-products which accompany the alcohol of genuine spirits.

Whisky is prepared by the distillation of alcoholic liquors from the fermentation of grain, potatoes, etc. Two well-defined types of still are in use—the pot still, which delivers all the volatile by-products, and the patent still, from which an alcoholic liquor comparatively low in volatile by-products is obtained. Pot still whisky possesses a characteristic aroma and flavour in consequence of these by-products or ‘impurities,’ as they are termed, and in time undergoes a change technically known as ‘ageing’; patent still whisky exhibits only slight ageing. Gin is a distilled liquor similarly prepared, and flavoured with juniper berries. Rum is the distillate of fermented molasses, and brandy is obtained by the distillation of wine.

The full examination includes a determination of specific gravity, alcohol, total solids, and organic acids, as already described.

The absence of mineral acids and salts is ascertained, and sugars, if present, are examined for reducing power and opticity. Flavourings and colouring matters require special analyses.

WINES

Wines consist of grape juice fermented under various conditions; the term has been extended to include the fermented juices of elderberries, rhubarb, raisins, etc. They contain alcohol, fixed and volatile ethers, invert sugar, tartaric acid, acetic acid, esters, and salts.

Wines are subject to fortification with methylated spirit,

dilution with water, addition of inferior alcoholic liquors, of mineral acids, flavouring and colouring matters. Contamination may also arise from the use of plaster of paris, alum, sulphur dioxide, etc., for clarification.

Alcohol. (Page 230.)

Total Solids. (Page 239.)

Mineral Acids

(Page 239.) Watering may sometimes be detected by the presence of nitrates which are entirely absent in pure wine.

Organic Acids

(Page 240.) The volatile acids are calculated as acetic, the non-volatile as tartaric. Tartaric acid in small quantities is a normal constituent; the non-volatile acids seldom exceed one-quarter of the volatile acids, and larger amounts suggest mineral acidity or added tartaric acid.

Ash

The ash of wine is determined by ignition of the residue from the evaporation of 100 cc.; it varies from 0.16 to 0.5 per cent.

The addition of calcium sulphate to wines, known as plastering, increases the SO_3 in the ash to an abnormal amount.

BEER

Beer is the fermented liquor of a carbohydrate decoction, flavoured with a natural wholesome bitter principle. It is manufactured from malt in two stages. In the preparation of the malt, barley is soaked in water and allowed to germinate, when diastase develops; the product is then heated at a low temperature in a kiln. The malt is digested with water at 30°C . for two to three hours, when the diastase converts the starch of the grain into maltose and dextrin. When saccharification is complete, the diastase is destroyed by steam boiling the extract or 'wort.' The hops are added at this stage. After a series of filtrations, to remove the hop husks and albuminous matter, the 'wort' is fermented with yeast. The final liquor is stored in bottles or barrels, and a secondary fermentation provides the natural aeration. Diastatic sacchari-

fication is not entirely relied on to produce the sugar for fermentation, and the addition of starch sugar, prepared by artificial hydrolysis of starch, has become common, and is regarded as legitimate.

The varieties of beer differ in the mode of preparation, and the concentration of alcohol.

The adulterations of beer include watering, fortification with spirits, and addition of mineral matter and artificial bitter principles.

The following determinations may be carried out in addition to those mentioned in the foregoing pages.

Specific Gravity

The carbon dioxide of the sample is removed by vigorous shaking, and the gravity is taken, usually by a Westphal balance.

Extract

The extract may be obtained directly by evaporating a weighed quantity of beer, or more conveniently from the 'excess' gravity, after removing carbon dioxide and alcohol. For direct weighing, only a small quantity (5 gm.) of beer is taken, in order to reduce the difficulties of drying, and is evaporated to dryness in a platinum basin on a steam bath, and then dried in a steam oven.

The excess gravity may be determined after boiling a sample to half bulk and making to the original volume with water, as directed on page 239, or from the residue from the indirect alcohol determination, after making to the original volume with water; this divided by four gives the extract.

Original Gravity of the Wort

The original gravity of the wort is calculated from the extract, and alcohol which has been obtained from the wort by fermentation. To calculate the loss of gravity due to fermentation, the 'spirit indication' is found by subtracting the gravity due to alcohol only (gravity of the alcoholic distillate made to original volume) from 1000. When the percentage of alcohol has been found indirectly, 0.16 is added¹

¹ Thorpe and Brown, *Analyst*, 1915.

to the spirit indication to allow for the difference in contraction of the alcohol in extract and aqueous solution. The spirit indication, referred to table below, gives the degrees of gravity lost by the wort during fermentation, and this figure, added to the gravity of the dealcoholised beer (boiled and made to original volume), gives the original gravity of the wort.

EXAMPLE (1) : From alcoholic distillate.

Specific gravity of alcohol distillate 988.9 (water=1000).

Spirit indication=1000-988.9=11.1.

Degrees of gravity lost (from table)=50.35.

Gravity of dealcoholised beer=1012.5.

Original gravity of wort=1012.5+50.35=1062.8.

(2) From loss of gravity on boiling.

Specific gravity of original sample after removing carbon dioxide=1010.5.

Specific gravity after boiling and making to original volume=1020.1.

Spirit indication=1020.1-1010.5=9.6.

Correction: 9.6+0.16=9.76.

Degrees of gravity lost (from table)=43.87.

Gravity of boiled beer=1020.1.

Original gravity of wort=1020.1+43.87=1064.0.

DEGREES OF GRAVITY LOST.¹

Spirit Indication.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.00	0.42	0.85	1.27	1.70	2.12	2.55	2.97	3.40	3.82
1	4.25	4.67	5.10	5.52	5.95	6.37	6.80	7.22	7.65	8.07
2	8.50	8.94	9.38	9.82	10.26	10.70	11.14	11.58	12.02	12.46
3	12.90	13.34	13.78	14.22	14.66	15.10	15.54	15.98	16.42	16.86
4	17.30	17.75	18.21	18.66	19.12	19.57	20.03	20.48	20.94	21.39
5	21.85	22.30	22.76	23.21	23.67	24.12	24.58	25.03	25.49	25.94
6	26.40	26.86	27.32	27.78	28.24	28.70	29.16	29.62	30.08	30.54
7	31.00	31.46	31.93	32.39	32.86	33.32	33.79	34.25	34.72	35.18
8	35.65	36.11	36.58	37.04	37.51	37.97	38.44	38.90	39.37	39.83
9	40.30	40.77	41.24	41.71	42.18	42.65	43.12	43.59	44.06	44.53
10	45.00	45.48	45.97	46.45	46.94	47.42	47.91	48.39	48.88	49.36
11	49.85	50.35	50.85	51.35	51.85	52.35	52.85	53.35	53.85	54.35
12	54.85	55.36	55.87	56.38	56.89	57.40	57.91	58.42	58.93	59.44
13	59.95	60.46	60.97	61.48	61.99	62.51	63.01	63.52	64.03	64.54
14	65.10	65.62	66.14	66.66	67.18	67.70	68.22	68.74	69.26	69.78
15	70.30	70.83	71.36	71.89	72.42	72.95	73.48	74.01	74.54	75.07
16	75.60

¹ Finance Act, 1914, Session 2 (Thorpe and Brown).

Acidity, Salts

A beer must be free from mineral acids, and the methods of examination described on page 239 are applied for their detection. Sulphuric acid may be present if starch syrup has been used in the brewing.

The presence of common salt, alum, and other mineral substances is determined by the ordinary methods of analysis, allowance being made for such amounts as may have been derived from the water used in brewing. For many of these estimations the methods described under water analysis may be employed.

Ash, Arsenic

A high ash indicates mineral addition. Copper and lead may be introduced from the metal portions of the brewing plant, and arsenic from glucose syrup. Arsenic is tested for as on pages 271-276.

Chlorine

The presence of high chlorine in the ash indicates the addition of salt to the beer. To estimate the chlorine, 100 cc. of beer is evaporated to dryness, and charred at a low temperature but not decarbonised. The char is extracted with boiling distilled water, filtered, and washed with hot water, and the filtrate is titrated with silver nitrate; the process and calculation follow those for chlorine in water (page 70).

UNCLASSIFIED ALCOHOLIC AND NON-ALCOHOLIC BEVERAGES

Many liquors are sold under a variety of fancy names, and their lack of definition allows great latitude in their preparation and manipulation. The analyst is able to make only a general statement of wholesomeness.

These liquors invariably contain alcohol derived from fermentation or from added alcoholic liquors or spirits. Sugars, citric and tartaric acids, saccharin, flavourings, colouring

matters, mineral acids and salts, may be found. The foregoing description of alcoholic liquor analysis provides methods which can be applied to these liquors. Determinations which may be made are alcohol, total acidity, volatile and non-volatile acids, mineral acids and salts, and poisonous metals.

LIME JUICE AND LEMON JUICE

Natural lime juice and lemon juice are similar in composition; they are on the market in both the raw and concentrated form. The addition of alcohol is not infrequent. A gravity of 1030 after dealcoholisation, and a minimum of 30 grains of citric acid per ounce, has been fixed as a standard by the Board of Trade. Preserved lime juice is extensively used as an antiscorbutic agent, especially on board ship, but it has been shown that it is quite useless for this purpose.¹

	Sp. Gr.	Free acid, chiefly citric.	Combined organic acid.
Raw juice, . . .	1030-1050	3.6 per cent.	0.24 to 0.48 per cent.
Concentrated juice, 1200-1400		25-50 per cent.	3 to 4 per cent.

The natural product has been largely displaced from the market by compositions of citric acid, etc., under various trade names, but when sold as lime or lemon juice they must be free from adulteration.

Mineral acids and salts are detected, and estimated, as on page 239. A genuine juice contains only traces of sulphates and chlorides. A small amount of sucrose is natural to lime and lemon juice.

Specific Gravity

The alcohol is removed from a measured volume of the sample by gentle boiling; the sample is cooled, made to the original volume, and examined with the Westphal balance.

Acidity

The sample is titrated with N/10 sodium hydroxide, using phenolphthalein as indicator. The acidity, in the absence of

¹ Chick, Hume, and Skelton, *Lancet*, November 1918.

mineral acids, is calculated as citric acid : 1 cc. N/10 NaOH = 0.0070 gm. citric acid.

Mineral Acids. (Page 239.)

Alcohol. (Page 230.)

Preservatives

Salicylic acid is commonly added as preservative. It can be detected and estimated by the method given on page 223.

VINEGAR

Vinegar is obtained by the acetous fermentation of a decoction of cereal grain or natural alcoholic liquors. It is characterised by the presence of acetic acid and small quantities of ethers, alcohols, sugars, acetates and tartrates, and extracts. In this country it is manufactured from malt, and on the Continent from wines, beers, ciders, molasses, sugars, and potatoes.

In many cases, in this country, starch syrup, molasses, low grade sugar, and gelatinised grain form the predominant portion of the fermented material, a little malt being added merely to give a claim to the name malt vinegar, and to impart a malt flavour. The carbohydrate extract is saccharified with malt extract, and fermented with yeast, and the alcoholic liquor (containing unfermentable dextrin) is subjected to the oxidising action of the *Mycoderma aceti* organism. The vinegar from the acetifiers is clarified by filtration, or by 'finings' of which potassium ferrocyanide appears to be the most commonly used (1 lb. per 1000 gal.).

It has been shown that potassium ferrocyanide in vinegar decomposes into Prussian blue, and it is presumed that hydrocyanic acid is formed; the use of potassium ferrocyanide obviously constitutes a possible source of danger.

The natural product is amber in colour, and to meet the public demand it is usually coloured with caramel.

Vinegar weak in acetic acid (below 3 to 4 per cent.) is liable to the growth of mould, to prevent which preservatives are

frequently added, or the vinegar is diluted to reduce the decomposable bodies present, and is then fortified with acetic acid. Addition of calcium bisulphite, salicylic acid, or pasteurisation at 70° C., are methods of preservation employed.

Distilled vinegar contains only acetic acid, water, and esters. Within recent years an increasing sale has been effected of vinegar from acetic acid, flavoured and coloured. The following standards have been defined by the Local Government Board, to control natural and artificial vinegars: ¹

‘Vinegar is derived wholly from alcoholic and acetous fermentation.’

‘Malt vinegar is derived wholly from barley or other cereals which have been saccharified with malt diastase only.’

‘Artificial vinegar is vinegar or substitute for vinegar containing any acetic acid not wholly the product of alcoholic and acetous fermentation.’

‘Any vinegar shall contain not less than 4 gm. of acetic acid in 100 cc.; not more than 0.0143 mgm. of arsenic in 100 cc.; no mineral acid, . . . etc.’

Vinegars fall into two classes, natural and artificial, and an analysis must indicate, as far as possible, that a vinegar sold as natural is not adulterated with artificial vinegar, and that a malt vinegar conforms to its definition.

The use of spirits and acetic acid, wood vinegar or pyroligneous acid, in the preparation of vinegar is indicated in the low extract and ash. Dilution and fortification with acetic acid is accompanied by the same effects together with a diminution of albuminoids. A pure malt vinegar is characterised by a comparatively high extract and a high phosphate value, 0.05 to 0.09 per cent. P_2O_5 . Dextrin may be present in malt vinegar in considerable amounts, but sulphates should little exceed that of the water used in manufacture.

Wine vinegars are characterised by tartar, usually from 0.25 to 0.5 per cent. They commonly have a yellow or red colour, and possess an alcoholic odour. Sugar vinegars give very small ash and phosphate values, and often contain more sulphates than the water of preparation. Spirit vinegars resemble sugar vinegars or artificial vinegar by their low ash and phos-

¹ *Local Government Board Annual Report, 1911-1912.*

phates ; they are often coloured with caramel, and flavoured with malt vinegar. The nitrogen of a malt liquor is naturally high, but is often lowered by the clarification ; the same applies to phosphates. Phosphates may also be increased by the addition of phosphate foods during brewing.

The following table compares the average percentage composition of some vinegars.

	Malt.	Wine.	Sugar.	Spirit.	Wood.
Specific gravity . . .	1017	1015	1017	1009	1007
Acetic acid . . .	5.5	6.5	3.9	5.9	4.0
Extract . . .	2.5	2.5	1.4	0.35	0.293
Phosphoric acid (P_2O_5)	0.085	0.048	Nil.	Nil.	0.002
Ash . . .	0.50	0.38	0.25	0.02	0.03

The adulterations of vinegar consist largely of sophistication with artificial vinegar, dilution with water, or admixture with cheap foreign makes. The addition of mineral acids is now rare. Arsenic may be present in malt, and is to be expected where starch syrup has been used. Copper and lead, from the plant, may be present, but this possibility is now almost eliminated by special arrangements.

Total Acidity calculated as Acetic Acid

10 cc. of the sample is made to 50 cc. with water, and titrated with N/10 sodium hydroxide (phenolphthalein indicator).

EXAMPLE :

10 cc. of vinegar diluted to 50 cc. required 70 cc. N/10 NaOH.

1 cc. N/10 NaOH = 0.006 gm. acetic acid.

Therefore 70 cc. N/10 NaOH = $70 \times 0.006 = 0.42$ gm. acetic acid.

Acetic acid = 4.2 per cent.

Mineral Acids

Mineral acids are detected and estimated as on page 239, and, if present, the acetic acid calculated from the total acidity must be corrected accordingly.

Total Original Solids

The acetic acid multiplied by 1.5 gives the grammes of extract from which it was formed, and this added to the extract

gives the original solids, without allowing for losses during fermentation.

EXAMPLE :

Extract converted to acetic acid $= 4.2 \times 1.5 = 6.3$ per cent.

Percentage of extract in vinegar $= 2.1$ per cent.

Total original solids $= 8.4$ per cent.

The alcohol, extract, albuminoid nitrogen, phosphate, and ash are determined as already described. Tests are made for copper, lead, and arsenic (pages 269-276).

BAKING POWDERS

BAKING POWDER consists of a mixture of suitable carbonate and acid substances, such that, on the addition of water, carbon dioxide is generated ; these are incorporated into a diluent, most commonly starch. The presence of baking powder in dough produces carbon dioxide, which imparts a porous structure to the bread, etc. ; in this way acting as a substitute for yeast. Flour to which the necessary proportion of baking powder has already been added is sold as 'self-raising flour.'

The composition of baking powder varies very considerably. Many cheap or inferior starches, casein, etc., may be used as diluent. Sodium bicarbonate is the most common carbonate constituent, but many others have been used. The acid ingredient is usually acid calcium phosphate, tartaric acid or cream of tartar. Calcium sulphate, to the extent of 15 per cent. or more, may be present owing to the use of inferior grades of acid calcium phosphate or deliberate admixture as weighting. The acid substance is sometimes coated with a film of semi-resistant material to protect it from atmospheric moisture, and to retard the liberation of the gas before baking. This film, which varies in thickness according to the time of storage required, may consist of wax, gelatine, albumen, etc. ; wax is most generally employed, applied in benzene solution. Further possible additions include fats and sugars.

The simple analysis of baking powder consists in an examination for carbon dioxide, starch, calcium, sulphates, phosphates, alum, and poisonous metals.

Starch

2 gm. of the sample is digested with cold water, filtered, and washed in the cold ; the residue is then transferred to a flask, and hydrolysed with dilute hydrochloric acid, as described

on page 227. The nature and origin of the starch may be determined from its microscopical character (pages 181-188).

Available Carbon Dioxide

The estimation of carbon dioxide is made gravimetrically in the Schrodter apparatus (Fig. 53). The apparatus is first washed, rinsed with alcohol, and dried in the steam oven with all taps removed. The apparatus is then allowed to cool in a desiccator. All stoppers are smeared with a thin film of resin cerate and replaced.

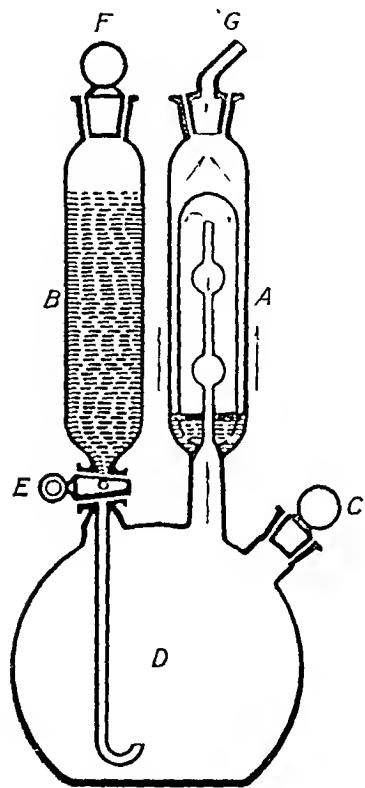


Fig. 53.

The tap E is closed, and the bulb B is half filled, by means of a pipette, with water; the stopper flange is dried if it has been wetted by this operation. Concentrated sulphuric acid is then run from a pipette through the exit G into the absorption bulb A, to cover the bubble holes, and drops of acid adhering to the exit tube are withdrawn by a spill of filter paper. 2 gm. of the sample is then introduced into the flask D, through the opening C, by brushing from glazed paper, and the stopper is firmly affixed into position. The apparatus, thus charged, is allowed to stand for half an hour on the pan of the balance (balance case closed)

and then weighed; it must not be touched with the hand during or immediately before weighing.

The stopper F is now slightly raised, and a portion of the water in B is allowed to run slowly into D by gently opening the tap E, the addition being so arranged that the liberated carbon dioxide bubbles through the washer A at a regular but not too great speed. When only a small quantity of water remains in B (it must not all be added), the tap E is closed and the stopper F is replaced. The apparatus is now *warmed*

for five minutes at 60° to 65° C. with frequent shaking, after which the exit tube G is connected, by means of a rubber tube, to an aspirator; the stopper F is removed and a small rubber stopper, carrying a tube connected to a sulphuric acid gas washer, is inserted in its place. The tap E is now opened, and a slow current of the dried air is allowed to pass through the apparatus for ten minutes. The apparatus is then disconnected, the stopper F is replaced, the whole is cooled in a desiccator, then allowed to assume the temperature of the balance case on the pan, and weighed as before. When transferring previous to weighing, the apparatus is held in a cloth.

The loss in weight between the two weighings represents the available carbon dioxide which has been expelled from 2 gm. of sample, and this is calculated to percentage.

The total carbon dioxide may be determined by using for the reaction a cold mixture of one volume of concentrated sulphuric acid and four volumes of water, instead of water as in the foregoing.

Calcium, Sulphates, and Phosphates

2 gm. of the sample is digested with 50 cc. of 5 per cent. hydrochloric acid (one volume of concentrated acid with five of water) at 30° to 35° C. for half an hour. The whole is filtered, washed, and the total filtrate cooled and made to 100 cc. (Stock solution.)

20 cc. of the stock solution is diluted to about 200 cc., 10 gm. of sodium carbonate is added, and the whole is gently boiled for thirty minutes. The mixture is filtered, and washed until neutral, and the filtrate discarded. The residue on the paper is dissolved by treating with 25 cc. of hot 5 per cent. hydrochloric acid in small portions and collecting the filtrate; the paper is washed. The total filtrate is made alkaline with ammonia, 10 cc. of 5 per cent. ammonium oxalate solution is added, and the estimation of calcium as CaO continued as described on page 99.

20 cc. of the stock solution is diluted to about 200 cc. and

boiled; to the boiling liquid 10 cc. of 10 per cent. barium chloride is added, and the estimation of sulphates as BaSO_4 is continued, as described on page 96.

Factor: BaSO_4 to $\text{CaSO}_4 = 0.5832$.

It has been suggested that calcium sulphate should not exceed 3 per cent. in baking powders, and 0.2 per cent in self-raising flours.¹

10 cc. of the stock solution is mixed with 25 cc. of concentrated nitric acid, and evaporated on a hot plate almost to dryness. To the cold residue 50 cc. of ammonium molybdate nitric acid solution (page 95) is added, and the whole warmed at 50°C . for half an hour. The precipitated ammonium-phospho-molybdate $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ is then filtered at once through an asbestos pad in a Gooch crucible, and washed until neutral to phenolphthalein. The pad and precipitate is then transferred to a conical flask, and 50 cc. of carbonate-free normal solution of sodium hydroxide is added and shaken. The excess sodium hydroxide is estimated by titrating with normal sulphuric acid, using phenolphthalein as indicator, and the sodium hydroxide consumed is obtained by difference: 1 cc. normal $\text{NaOH} = 0.00312 \text{ gm. P}_2\text{O}_5$.

Arsenic and Lead

Arsenic and lead are detected and estimated as on pages 270-276.

Alum. (Page 178.)

¹ Report to the Local Government Board by Dr. J. M. Hamill, Food Reports. No. 13, 1911.

TEA, COFFEE, COCOA, AND CONDIMENTS

THESE substances are characterised by their seed or leaf structure. The greater bulk is imported, and Government control at the ports of entry has practically eliminated adulteration. Sophistication of these vegetable products is most readily detected by the microscope, which takes priority over chemical methods in examination for foreign vegetable and mineral matter. The following are some general methods of chemical examination.

Moisture

10 gm. of the finely divided material is dried at 100° C. until constant in weight.

Ash

Total Ash.—10 gm. is ignited at a low heat in a platinum basin and weighed.

Soluble Ash.—10 cc. of distilled water is added to the total ash in the basin and warmed on a steam bath; the liquid is then decanted into a filter. The residue is washed with warm water, and the washings are decanted into the filter; the filter is washed, returned to the basin, and ignited. The residue is the insoluble ash, and the loss in weight of the total ash is the soluble ash.

Alkalinity of the Ash.—The total filtrate from the above is collected in a 250 cc. measuring flask, cooled, and made to the standard volume; an aliquot part is titrated with N/10 H_2SO_4 using methyl orange as indicator. The alkalinity is expressed as percentage of potassium oxide of the original material: 1 cc. N/10 H_2SO_4 = 0.00471 gm. K_2O .

Sand

The insoluble ash is extracted with 10 cc. of hot 10 per cent.

hydrochloric acid ; the extract is decanted and filtered, and the filter, after washing, is returned to the dish and ignited. The residual ash is returned as sand.

Fat

5 gm. of the thoroughly dry material is extracted in a Soxhlet apparatus with dry ether ; the extracted fat is dried at 100° C., and weighed.

Fibre

The residue from the ether extract is transferred to a flask, and digested at 100° C. for one to two hours with 200 cc. of distilled water and 20 cc. of 10 per cent. H_2SO_4 . The fibre is allowed to settle, and the liquid is decanted through a weighed filter ; the extraction is repeated at least twice. Finally the fibre is washed into the filter, dried at 100° C., and weighed.

Starch

The sample is first freed from fat in the Soxhlet apparatus and is then digested with cold water for at least twelve hours to remove sugars. The starch in the washed residue is extracted with boiling water, and is determined by hydrolysis to glucose.

Sugars

The cold-water extract from above is examined for sugars by the methods already described.

Protein

The total nitrogen is obtained by Kjeldahl's method ; the nitrogen of any alkaloid is subtracted, and the factor 6.25 used to convert the remainder to protein.

TEA

In the preparation of tea, the leaves of the tea plant are withered in a warm room, and rolled to remove the juice. The product is then allowed to ferment, when it changes from a green to a brown-black colour. It is then roasted and graded.

Caper tea is the tea dust residual from the preparation of the leaf, covered with gum arabic and faced. The composition of tea varies slightly with its origin, and is characterised by the presence of the alkaloid theine (caffeine). The adulterations formerly practised included the addition of exhausted leaf, foreign leaf, foreign astringent, mineral matter, and facing. Foreign leaf, fibre, and mineral matter may be revealed by a microscopical examination. Exhausted leaves cannot be so readily distinguished, but a low percentage of theine, of which they are practically destitute, and a low soluble ash, provide means of detection.

An analysis includes the following estimations.

Moisture

The leaf is dried at 100° C., and the loss in weight is ascertained.

Extract

The dry leaf is boiled with fifty parts of water for one hour, drained through a filter, and re-extracted until the liquor is only faintly coloured; the extract is estimated by the loss in weight of the leaf after filtering, washing, and drying. The extract of genuine tea is 35 to 50 per cent.; low figures indicate possible sophistication with exhausted leaves.

Insoluble Leaf

The residue from the above is the insoluble leaf and should not be above 60 per cent.; high values suggest adulteration with exhausted leaf.

Ash

(Page 255.) The presence of exhausted leaves lowers the soluble ash (4 per cent. in genuine leaf and 0.5 per cent. in exhausted leaf) and the alkaline ash (2 per cent. K_2O in genuine leaf and 0.3 per cent. K_2O in exhausted leaf). Mineral adulterations may be tested for in the ash if it exceeds 8.0 per cent.

In addition the following estimations are occasionally made.

Theine

5 gm. of the tea is boiled for two hours under a reflux condenser with 250 cc. of water, filtered, and washed. The extract is evaporated to dryness, taken up with 100 cc. of water, and clarified with alumina cream; the liquor is filtered with washing, and evaporated to small bulk. About 10 gm. of finely powdered porous plate, previously washed and ignited, is added, and the mixture is dried at 100° C.; the theine is extracted with chloroform, from the mass, in a Soxhlet, and weighed.

Tannin

The tannin of the genuine leaf varies from 10 to 15 per cent., and in the exhausted leaf it is about 2 per cent. It is estimated by oxidation with standard iodine solution.

5 gm. of the sample is extracted with three successive portions of boiling water, filtered, and the cooled filtrate is made to 1 litre. Aliquot portions of this extract are titrated with N/10 iodine solution, using fresh starch solution as indicator. 1 cc. N/10 iodine solution = 0.0021 gm. tannin.

The tannin should not be less than 6.0 per cent. in a genuine sample.

COFFEE

Roasted coffee seeds are sold either whole or ground. The latter form gives greater scope for adulteration, but imitation beans are known. The only adulteration common in present times is the admixture of chicory with ground coffee; this is illegal when not declared.

Chicory present in coffee may be seen by microscopical examination. Other adulterations can be best observed and identified by the same method.

Chicory

Jones' Method

5 gm. of the sample, previously dried at 100° C., is boiled with 200 cc. of water for five minutes. After settling, the extract

is decanted through a gauze filter; the residue is further boiled with 50 cc. of water for five minutes, and strained as before. The total extract is cooled, made to 250 cc., mixed, and filtered through a dry filter; 50 cc. of the filtrate is evaporated to dryness, dried in the steam oven, and the extract is calculated to percentage of the original sample.

Pure coffee gives an average extract of 24 per cent.; chicory an average extract of 70 per cent. Then the percentage of chicory

$$= \frac{(\text{percentage of extract} - 24) \times 100}{70 - 24}.$$

Gravity of Extract Method

10 gm. of the sample is boiled with 100 cc. of water for five minutes; the whole is filtered through a small gauze filter, and then through filter paper, into a 100 cc. measuring flask. The residue is washed with a small quantity of water until the total filtrate, after cooling, reaches the mark. The extract is mixed, and the specific gravity is taken by the Westphal balance; from this the percentage of chicory is calculated as follows:

Maximum gravity of a 10 per cent. extract of coffee is 1010.

Minimum gravity of a 10 per cent. extract of chicory is 1025.

Then percentage of chicory = $\frac{(\text{gravity of extract} - 1010) \times 100}{1025 - 1010}$.

C O C O A

The cocoa seed is partially fermented, roasted, and, after removing the shell, is deprived of some of its fat by pressing, and finally ground for sale as commercial cocoa. The powdered cocoa or soluble cocoa sold under various names is reduced to a finer state of division by special milling and may be treated with alkalies; it should not contain alkali over 3 per cent., calculated as sodium carbonate. These preparations very generally contain added starch and sugar.

The characteristics of pure cocoa are its fat (cocoa butter), theobromine, and small quantities of theine. The chief adulterations are shell, starch, and sugar, but mineral additions have been recorded.

The Cocoa Powder Order, 1918, made it illegal to manufac-

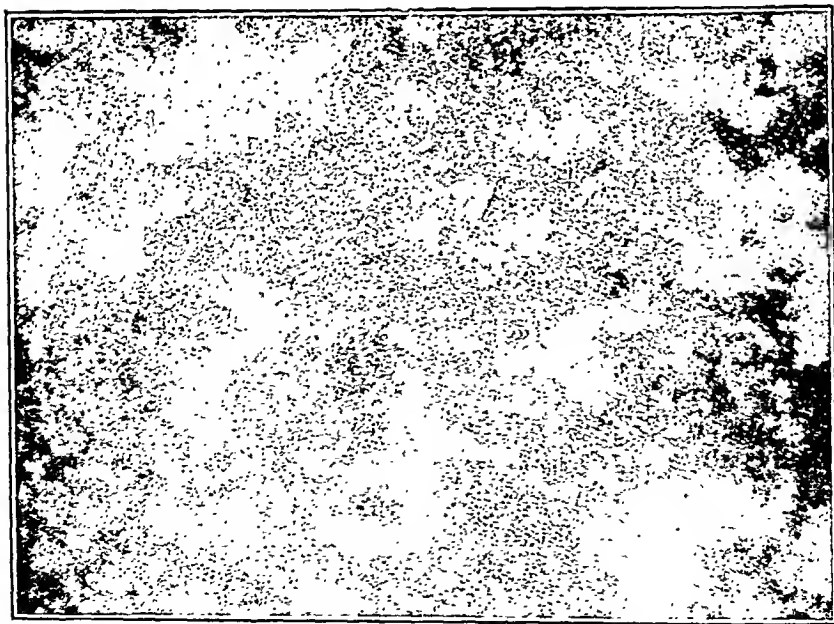


Fig. 54.—Pure Cocon. ($\times 160$.)



Fig. 55.—Cocoa adulterated with Arrowroot Starch. ($\times 160$.)

The black patches in these photographs are pieces of shell. The large size of the arrowroot starch grain (Maranta) makes its presence very evident even with such a comparatively low magnification.

ture cocoa not conforming to one of two standards: Grade A containing cacao-bean shell not exceeding 2 per cent., and Grade B shell not exceeding 5 per cent. There is no known method of analysis for estimating shell to distinguish between these figures, and the order became practically a dead letter.

Cold-water Extract

The sample is digested with cold water for twenty-four hours. A cold-water extract over 18 per cent. indicates added sugars, and the extract is examined for the same by the methods described.

Starch

Foreign starches can be detected only by the microscope, as the natural starch fluctuates considerably in quantity.

CHOCOLATE

For the purpose of making chocolate, the cocoa is ripened by moist fermentation, during which it loses its bitterness and acquires a pleasant aromatic flavour. The product is made into a paste with water, mixed with flavourings, sugar, etc., and pressed into moulds. Milk chocolate is compounded of chocolate, sugar, milk powder or milk products, and cocoa or other butter.

The analysis of chocolate includes the estimation of sugars (including lactose from milk products), fat, and starches.

COCOA TEAS

The shell from the cacao-bean is sold for the preparation of a decoction after the manner of tea. On account of its very low cost it has been used by the poorer classes in Ireland, where it is known as 'miserables.' During the war and the consequent shortage of tea, this material was widely offered for sale in the United Kingdom under fancy names conveying no suggestion of its real nature, and at grossly inflated prices. With the issue of the Cocoa Powder Order, 1918, fixing the maximum price at 6d. per lb., these preparations were rapidly withdrawn.

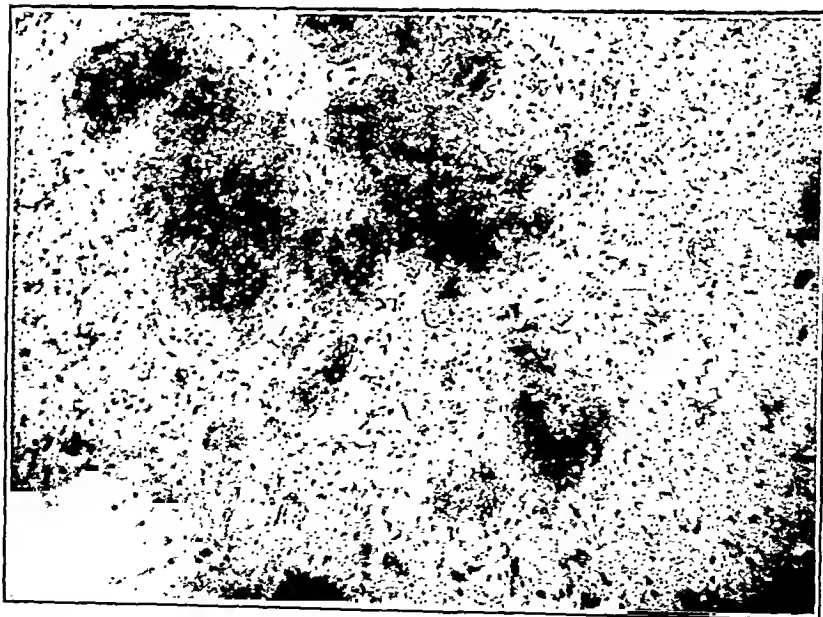


Fig. 56.—Pure pepper, ground. ($\times 160$.)



Fig. 57.—Pepper, ground, adulterated with Maize Starch. ($\times 160$).

The illustration of pure pepper shows nothing characteristic, but the negative evidence makes it useful for comparison with that of the adulterated sample. Polygonal and rounded starch grains with a very distinct central hilum are quite evident, and the provisional diagnosis of the presence of maize starch was readily confirmed on examining with a higher magnification.

PEPPER

Pepper contains piperin, starch, and fibre, etc., and is sold in two varieties, black and white; the former is the whole and the latter the decorticated seed. Added starch is a common adulteration. The examination of pepper is essentially microscopical; it is usual, however, to estimate the ash.

Ash

The ash of black pepper should fall within the limits of 3 and 5 per cent., with not more than 2 per cent. insoluble in 10 per cent. hydrochloric acid; that of white pepper should be between 1 and 3 per cent., with a limit of 1 per cent. insoluble in acid.

Mineral adulteration may be tested for in the ash.

Fibre

(Page 256.) The fibre averages 12 per cent. in black and 4 per cent. in white pepper.

Nitrogen

The piperin of pepper is not decomposed by the Kjeldahl method, and where required the nitrogen is estimated by combustion.

Starch. (Page 227.)

MUSTARD

Mustard is the sifted, ground seed of the mustard plant, and is characterised by the presence of mustard oil; it contains no natural starch. Added starch is a common adulteration. The ash should not exceed 5 per cent. An examination is mainly microscopical, but the following determinations are useful.

Starch

Starch is determined, after extraction with ether, as described on page 227.

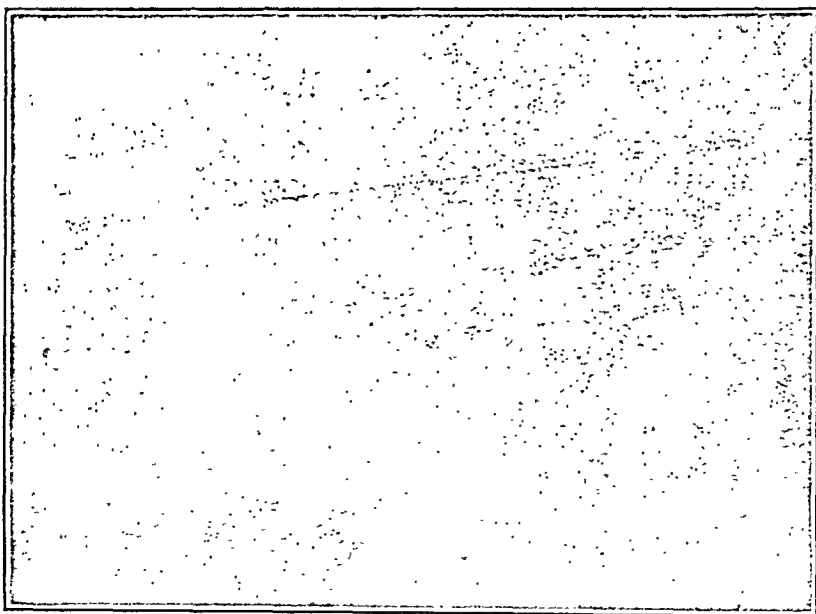


Fig. 58.—Pure Mustard. ($\times 730$.)



Fig. 59.—Mustard diluted with Wheat Starch.
($\times 730$.)

The wheat starch is very evident in the centre of the field. The negative evidence in the photograph of pure mustard makes it useful for comparison.

Turmeric detection

The mustard is moistened with dilute ammonia solution, and examined with a pocket lens; red specks and stains show foreign matter. An alcoholic extract of the sample gives the boron reaction if turmeric is present.

Mustard Oil

The sample is extracted with dry ether in a Soxhlet apparatus, and the extracted oil, after evaporation of the ether, is dried at 60° C. The oil in pure mustard averages 30 per cent., and 18 per cent. in the manufactured products.

TABLE SALT

Table salt is refined sodium chloride in small crystals obtained from brine by rapid evaporation near the boiling-point. Impure salt cakes on exposure to air, owing to the presence of calcium and magnesium chlorides which are deliquescent. Table salts containing added inorganic phosphates are largely used.

Moisture

10 gm. of the sample is heated at 100° C. until constant in weight.

Chlorine as Sodium Chloride

Solutions required:

Decinormal solution of silver nitrate containing 16.989 gm. per litre: 1 cc. = 0.005846 gm. sodium chloride or 0.003546 gm. chlorine.

Solution of pure potassium chromate, free from chlorides, as indicator.

Process:

5 gm. of the sample is dissolved in water, and the solution is made to one litre. 25 cc. of this solution is titrated with the decinormal silver nitrate solution, and the chlorine present is calculated to percentage of sodium chloride in the sample.

EXAMPLE :

5 gm. of sample in one litre. 25 cc. of solution requires 19.7 cc. of N/10 AgNO_3 .

1 cc. N/10 $\text{AgNO}_3 = 0.005846$ gm. sodium chloride, \therefore 19.7 cc. N/10 $\text{AgNO}_3 = 0.11512$ gm. NaCl.

$= 0.11512$ gm. NaCl in 25 cc. of solution $= 4.605$ gm. in 1 litre of solution.

$= 4.605$ gm. NaCl in 5.0 gm. of sample.

Therefore chlorine, calculated as sodium chloride $= 92.10$ per cent.

Phosphate

Phosphate is estimated in the above salt solution in the same manner as described on page 177, using a standardised solution of uranium acetate, and is calculated to percentage of P_2O_5 in the original sample.

Insoluble, Iron, Aluminium, Calcium, and Magnesium may be estimated as described on page 98.

THE DETECTION AND ESTIMATION OF METALLIC POISONS IN FOOD- STUFFS

TIN

CANNED foods often contain tin in quantities which vary with the nature of the materials used, and the method of closing the receptacle ; the amount present increases with the age of the sample. A limit of 2 grains of tin per pound (28.56 milligrammes in 100 gm.) has been proposed.¹

Estimation: Schryver Methods ²

Gravimetric

The gravimetric method is employed when large quantities are suspected to be present.

25 gm. of the sample is mixed, in a Kjeldahl flask, with 25 gm. of potassium sulphate, and 25 cc. of concentrated sulphuric acid previously diluted with 100 cc. of water. The whole is gently concentrated, and charred. 25 cc. of concentrated sulphuric acid is added, and decarbonisation is completed ; frothing is avoided as much as possible, and the contents of the flask are not allowed to become dry. The residue is then diluted with 300 cc. of water, and sulphuretted hydrogen is passed through until the liquid is saturated. The flask is corked, and allowed to stand overnight. The whole is then warmed, and the precipitate of sulphide and sulphur is filtered, and washed with warm water. In order to separate siliceous matter, etc., in the residue, the stannous sulphide is dissolved by adding 10 cc. of hot 10 per cent. sodium hydroxide solution to the filter, and washing through with hot water. The sulphide is reprecipitated from the filtrate by acidification with acetic acid ; it is then filtered, washed, dried, ignited, and

¹ Local Government Board Inspector of Foods, Report No. 7, 1908.

² *Ibid.*

weighed as oxide in the usual way. One part of stannic oxide (SnO_2) represents 0.7876 parts of tin.

Colorimetric

Tin as stannous salt can be estimated by means of the violet coloration it gives with dinitrodiphenylaminesulphoxide.¹

Solutions required:

0.2 gm. of dinitrodiphenylaminesulphoxide is dissolved in 100 cc. of N/10 sodium hydroxide solution, and filtered.

A standard solution of stannous chloride containing 0.714 gm. of tin in 500 cc. is prepared by dissolving this weight of pure tin in a few cc. of concentrated hydrochloric acid, and diluting to one half litre. 1.0 cc. of this solution = 1.428 mgm. tin, and each cc. required for 10 gm. of sample represents one grain of tin per pound.

Ferric chloride solution, 5.0 per cent.

Process:

The destruction of the organic matter is effected as described in the case of the gravimetric estimation of tin; for the colorimetric estimation, smaller quantities of the sample may be taken.

10 gm. of the sample is concentrated and suitably charred with 10 gm. of potassium sulphate and 10 cc. of sulphuric acid diluted with 50 cc. of water. Additional sulphuric acid, from 10 to 30 cc., according to the amount of organic matter present, is added and the decarbonisation is completed. The clear residue is diluted to 100 cc., and, without filtration, is saturated with sulphuretted hydrogen. After several hours the precipitate is filtered, and washed. The filter paper containing the washed precipitate is transferred to a test tube, and is extracted with 5 cc. of boiling concentrated hydrochloric acid. The whole is then filtered through a small conical Büchner funnel connected to a filter pump, and sucked as dry as possible, and squeezed with a flattened rod. The filtrate is collected in a test tube contained in a Büchner receiver. The residue is then washed with three portions of 2 cc. of hot con-

¹ Liebig's *Ann.*, 230, p. 116, 1885.

centrated hydrochloric acid. The test tube is closed with a cork carrying a short inlet tube by means of which a stream of carbon dioxide is passed close to the surface of the solution and displaces the air in the tube. Whilst the solution is still hot, the cork is raised, and a piece of zinc foil weighing 0.75 to 1 gm., and about 2 inches long and $\frac{1}{2}$ inch wide, is added; the cork is immediately replaced, and the passage of the carbon dioxide continued throughout the test. As soon as the last traces of zinc are dissolved, 2 cc. of the dinitrodiphenylamine-sulphoxide solution is added, and the mixture is warmed to boiling. It is then cooled, diluted to 100 cc. with water, filtered, and a drop of ferric chloride solution is added. The presence of tin is indicated by the formation of a violet coloration. When the test is carried out as above, one-tenth of a grain of tin per pound gives an appreciable colour, while one grain per pound gives a deep purple, and in this case it is advisable to make colour measurements with only a portion of the solution, obtained after destruction of organic matter. Amounts above one grain per pound are best estimated by the gravimetric method.

The colour obtained is compared with standard colours of known amounts of tin. 1.0 cc. of the standard tin solution contains 1.428 mgm. of tin, which in 10 gm. of food is equivalent to one grain of tin per pound; to prepare standards of less equivalents than 1 grain per pound, 0.75 cc., 0.5 cc., and 0.25 cc., corresponding to 0.75, 0.5, and 0.25 grain per pound respectively, are measured into boiling tubes. To each is added 10 cc. of concentrated hydrochloric acid, and a standard piece of zinc foil. The reduction in carbon dioxide atmosphere, dilution, and coloration with the reagent, is proceeded with as in the case of the sample. The sample colour is now estimated by comparison with these standards.

COPPER

20 gm. of the sample is weighed into a basin, dried, and ignited at a gentle heat. To the ash, 5 cc. of 20 per cent. nitric acid is added, and the whole is evaporated to dryness on the steam bath. The residue is taken up with water, and again

evaporated to dryness; this operation is repeated. The residue is now taken up with 5 cc. of 5 per cent. sulphuric acid. The whole is made alkaline with strong ammonia, and transferred to a centrifuge tube; the basin is rinsed with a few cc. of water into the tube. The whole is centrifuged, and the clear liquid is pipetted (see page 149) into a 100 cc. measuring glass. The residue in the tube is mixed with water and again centrifuged, and the clear liquid is added to the quantity previously obtained, and the whole made to 100 cc. A blue coloration indicates the presence of copper, and by comparison with standard ammoniacal copper solutions, the amount is determined; the procedure is similar to the colorimetric methods described in water analysis.

In this process the solutions are not filtered through filter paper, as the copper may be partly or entirely removed by adsorption in the cellulose.

LEAD

Solutions required:

Sulphuric acid, 20 per cent.

Ammoniacal ammonium acetate, 5 gm. of ammonium acetate in 100 cc. of ammonia (1 in 3).

Potassium cyanide, 10 per cent.

Ammonium sulphide. Fresh colourless reagent.

Process:

10 to 50 gm. of the sample is mashed into a pulp, and intimately mixed with 5 to 25 cc. of sulphuric acid. The whole is heated, gently at first, and finally completely ashed. The sulphated ash is boiled for a minute with a small quantity of ammoniacal ammonium acetate solution. The liquid is centrifuged, and the residue is separated and washed, as described for the estimation of copper. To the total filtrate 5 cc. of potassium cyanide solution is added; the whole is made to 100 cc., and mixed. In this solution the lead is estimated as in water (page 91), and calculated to percentage or grains per pound of the original sample. A blank test should

always be made with the reagents to make certain of their purity.

In Dr. A. W. J. MacFadden's report to the Local Government Board on lead and arsenic in tartaric acid, citric acid, and cream of tartar (1907), it is suggested that the permissible limit for lead in these substances should be 0.002 per cent.

ARSENIC, ANTIMONY, AND MERCURY

The most suitable general test for arsenic, antimony, and mercury is that of Reinsch. The Marsh test for arsenic and antimony, described later, is more sensitive, but has the disadvantage that it fails to detect arsenic and antimony in organic combination without previous treatment requiring considerable time. In either test rigorous control to ensure the absence of these metals from the reagents is essential.

Reinsch Test

If the sample is liquid about 100 cc. is taken; if solid, 10 to 50 gm. in small pieces with about 100 cc. distilled water. 25 cc. of arsenic-free concentrated hydrochloric acid, and a piece of bright copper foil (pure by electrolysis), about 0.7 cm. square, is added; the whole is allowed to boil and kept just boiling for three-quarters of an hour. At the end of this time the copper is removed, washed with water, and afterwards with ether. If arsenic or antimony is present, the copper will hold a dull dark deposit, varying in degree with the amount present; mercury imparts its characteristic bright appearance, which is made more apparent on rubbing. Tin, silver, bismuth, gold, and platinum, if present, will also be deposited on the foil, but only an arsenic, antimony, or mercury deposit sublimes on heating in the continuation of the test. The copper with its deposit is carefully dried with filter paper, and washed with ether; it is then cut into small pieces. Examination is now made to determine whether the deposit sublimes, and if it does so, the sublimate is examined microscopically. One of two methods can be employed to effect the sublimation.

(1) The pieces are gently heated in a thin glass flat sublimation tube as devised by Dixon Mann; the sublimate remains in the cold part of the tube. (2) Delépine's method: with a piece of pure copper foil a cone about 1 cm. high and of the same diameter is made; this rests, open end upwards, in an iron plate having one hole about 0.7 cm. in diameter. The pieces are placed in this, a cover glass is laid on the cone, and any sublimate collected after the application of very gentle heat. It is advisable to make certain of the absence of arsenic from the cone by making a blank test previous to adding the deposit. With a rather high magnification (about 400) the microscopical appearance of the sublimates from the three metals are quite different; a dark ground illumination is an advantage. Arsenic trioxide under suitable conditions gives large octahedral crystals, but frequently the crystals are quite small, and close examination is necessary to see the crystalline appearance. Antimony trioxide is seen as an amorphous substance, very minute particles like so many pin points. Mercury gives opaque globules of varying size. A blank test of the reagents should always be made simultaneously.

Marsh-Berzelius Test

The principle of the method is that hydrogen is generated, and in the presence of arsenic or antimony, arsenious or antimonous hydrides respectively are formed. The metals are readily obtained from their hydrides by decomposition on heating.

Reagents required:

Concentrated sulphuric acid, arsenic-free.

Zinc, arsenic-free.

Lead acetate, 10 per cent. solution.

Calcium chloride, dry, previously moistened with concentrated hydrochloric acid and ignited.

Bleaching powder, 2 per cent. solution.

Apparatus required:

A convenient form of the apparatus required is that illus-

trated in Fig. 60, but any similar arrangement will give satisfactory results.

Hydrogen is generated in the flask D, and after passing through the absorption tube A, the gas can be heated in the hard glass tube B or ignited at G. When the issuing hydrogen is ignited the flame may melt the glass; this can be prevented by enclosing the end of the tube in a small piece of projecting platinum foil. The part of the tube heated by the bunsen is covered with iron gauze, as shown in the figure, to cause an even distribution of heat, and to prevent the tube bending. The tube is supported on the flame steadier. The reagents and sample are added to the flask through the stoppered funnel C.

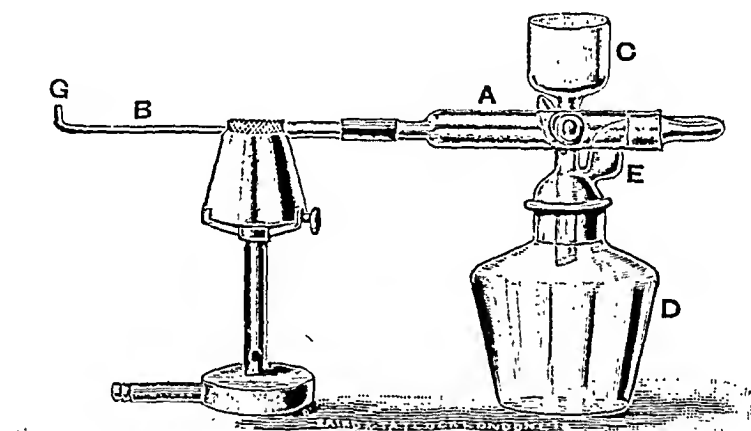


Fig. 60.

The tube A is prepared in the following manner before use: Commencing at the narrow end, a small plug of cotton wool is inserted, then pieces of calcium chloride, another piece of cotton wool, then a small roll of absorbent paper previously soaked in lead acetate solution, and finally another piece of cotton wool; a plug of cotton wool is also placed in the bent tube E. It is important that each should be packed loosely to allow easy passage of the gas. The lead acetate paper absorbs sulphuretted hydrogen and the calcium chloride absorbs moisture.

Process:

It is first necessary to make quite sure of the absence of arsenic or antimony from the reagents.

About 10 gm. of zinc is placed in D, about 35 cc. of distilled water is added, the stopper arrangement inserted, and the tube A, prepared as already described, is connected to E. The hard-glass tube B is then attached to A and supported on the bunsen burner. Sulphuric acid is introduced into the funnel C. By opening the stopcock the acid is allowed to run into the flask, in small quantities at a time; the stopcock is shut after each addition. Hydrogen is generated, slowly at first, and, after the elapse of a short time to allow the air in the apparatus to be expelled, is ignited at G. Hydrogen and air form an explosive mixture, and this precaution must be carefully observed; explosion may also be caused by allowing too much acid to enter the flask, with the consequent generation of an excessive quantity of hydrogen.

Arsenic or antimony in the reagents will become evident by the formation of a black-brown stain when the flame at G is allowed to impinge upon a cold porcelain surface. If the tube B is now heated, the arsenic or antimony will be deposited in the tube, producing a dark-coloured ring. The metals must not be considered absent until a negative result is obtained after passing hydrogen (further quantities of acid are added as necessary) and heating the tube for at least thirty minutes. The burner of the apparatus is extinguished, and the deposition tube allowed to become cold. If the reagents have been found to be free from arsenic, the examination of the sample is now made.

If the sample is liquid and the arsenic or antimony is in inorganic combination and free from much organic matter, it may be added direct to the apparatus, otherwise preliminary treatment is necessary, as follows:—

25 to 100 gm. of the sample in small pieces, in a porcelain basin, is covered with a mixture of equal volumes of sulphuric acid and water, and heated over a rose burner until thoroughly charred. The residue is taken up with the concentrated sulphuric acid diluted 1 in 10, boiled, and filtered; a clear and not too dark-coloured solution should be obtained. A crystal of potassium metabisulphite is added to the filtrate, which is then boiled until no smell of sulphur dioxide is apparent; it may be concentrated further if necessary.

Small quantities of the sample and of sulphuric acid, when direct examination is possible, or the solution from the above treatment, are added from time to time (care being taken to prevent the entry of air) to maintain a steady evolution of hydrogen for a minimum of forty-five minutes. After the flame at G has been allowed to impinge on a piece of cold porcelain, the burner is relit to obtain any deposit in the tube B. Sulphur from the acid, by reduction, may appear as a yellow deposit, and must not be confused with a brown to black deposit of arsenic or antimony; careful examination with a hand lens should be made in such cases, as the sulphur tends to mask a deposit of these metals.

Arsenic and antimony can be differentiated in the following ways:—

(1) The stain on porcelain is treated with bleaching powder solution; that from arsenic is soluble, that from antimony is insoluble.

(2) If the deposit in the tube is arsenic, deposition takes place entirely in that part furthest away from the flask; if antimony, deposition takes place on both sides of the heated part.

(3) The portion of the tube containing the deposit is cut off. Air is blown through to displace hydrogen (and sufficient to remove any moisture), and the ends are sealed. If the tube is now gently heated, the sublimate of arsenic or antimony trioxide can be determined by microscopical characters already detailed (page 272).

The test can be made roughly quantitative if the process is carried out under standard conditions, and the deposit compared with similar deposits prepared from standard solutions. 1 gm. of As_2O_3 or Sb_2O_3 is dissolved in water with a few cc. of arsenic-free concentrated hydrochloric acid, and made to 1 litre: 1 cc. contains 1 mgm. This solution is diluted 1 in 1000, then 1 cc. of the diluted solution = 0.001 mgm. With various quantities of the dilute solution, separate deposits equal to definite amounts of arsenic or antimony are obtained in tubes, which are then sealed full of hydrogen. By comparing the deposit from a weighed quantity of sample with the standard tubes, an approximation of the amount of arsenic or antimony present is arrived at.

The Royal Commission on Arsenical Poisoning, in their final report, 1903, recommended that no substance used in food, whether intended for consumption alone or mixed with other substances, should contain more than $\frac{1}{100}$ grain of arsenic per lb. if solid (14.28 mgm. per 100 gm.), or per gallon, if liquid (1.428 mgm. per 100 cc.).

DISINFECTANTS

DISINFECTANTS are defined as germicides, or reagents which kill bacteria, and are to be distinguished from antiseptics which may only inhibit their growth. Disinfectants are widely employed as germicides, deodorants, and for the prevention of infection, and antiseptics are used as preservatives in food. The germicidal power of a disinfectant is determined bacteriologically, but a chemical analysis gives the available reagent in a sample, and some indication of the composition of proprietary products. The following disinfectants are in very general use.

Coal Tar Disinfectants

Coal tar disinfectants are prepared from portions of the distillate of coal tar, and depend for the germicidal power on the higher homologues of phenol and small amounts of phenol. The homologues of phenol have much higher disinfectant powers than phenol. The preparations, which form dark-coloured syrups, are emulsified with potash soap or mixed with gelatine or gum. They are perhaps the most widely used disinfectants, and are on the market under a variety of proprietary names. The germicidal co-efficient varies according to the method of preparation, and to the many admixtures which are made. The chemical examination is conveniently made by the *Lancet* acetone-baryta (L.A.B.) method, as follows :—

Coal Tar Disinfectants containing Soaps.—10 gm. of the syrup is extracted by shaking with 100 cc. of water; 15 gm. of barium hydroxide is added, and the whole is heated on a steam bath for one half-hour under a reflux condenser. The mixture is cooled, and the liquid is decanted through a glass wool or asbestos wad in a filter funnel.

The residue is washed with hot water, and retained for further examination. The total filtrate is made to 500 cc. and mixed, 100 cc. of the filtrate is acidified with hydrochloric acid, and the liberated phenolic bodies are extracted with two portions of ether; they are separated from the ether by evaporation in a weighed basin, and weighed. This extract is then dissolved in a small quantity of 5 per cent. sodium hydroxide, and an excess (about 100 cc.) of a standardised solution of bromine of about normal strength in sodium hydroxide is added. The solution is acidified with hydrochloric acid, 10 gm. of potassium iodide is added, and the excess of iodine is titrated with normal sodium thiosulphate solution: 1 cc. = 0.0799 gm. Br. One gramme of phenol requires 5.1 gm. of bromine; the homologues of phenol, having a higher molecular weight, require less. Thus if the bromine absorbed corresponds to less phenol than is extracted with ether, and weighed in the above operation, the homologues of phenol are present, and phenol may be absent.

The barium precipitate from the above filtration is thoroughly extracted with acetone to dissolve neutral hydrocarbons which may be present, and the insoluble soaps and resins are filtered, and washed with acetone. These are then shaken with 10 per cent. hydrochloric acid, and the fatty acids extracted with ether, and, after evaporation of the ether in a weighed basin, are weighed. They represent the soaps present in the sample.

Water is estimated by shaking 25 gm. of the sample with 10 cc. of a 10 per cent. sulphuric acid solution, and 25 cc. of petroleum ether. The mixture is allowed to separate in a measuring cylinder, and the volume of the aqueous layer, above the 10 cc. of acid added, represents the water in the sample taken.

The alkali in the disinfectant is estimated by the alkalinity of the ash.

Coal Tar Disinfectants not containing Soaps.—In the absence of soaps, gums or gelatines are usually employed as an emulsifier of the tar product, and in the analysis the baryta saponification is not required. The gum or gelatine is separated by shaking 10 gm. of the sample with

50 cc. of acetone, filtering, and washing the residue with acetone. The residual gum or gelatine is weighed. The acetone extract is shaken with an equal volume of 10 per cent. sodium hydroxide solution, and any neutral oil which is precipitated is separated. The alkaline solution is filtered, and made to 500 cc. 100 cc. of this solution is examined for phenolic bodies by extraction with ether after acidification, and by bromine as in the previous process.

'Chloride of Lime'

The germicidal power of chloride of lime or bleaching powder depends on the available chlorine it contains; this should be 30 to 35 per cent.

Reagents required:

Decinormal Sodium Arsenite.

4.948 gm. of As_2O_3 and 20 gm. of sodium carbonate, with about 500 cc. of water, are heated, over a rose burner, in a beaker covered with a watch glass. When solution is complete, the watch glass is washed with water and the washings are collected in the beaker; the whole is cooled, and made to one litre: 1 cc. = 0.003546 gm. Cl.

Starch iodide papers as indicator.

Process:

About 5 gm. of the sample is accurately weighed in a weighing bottle, made into a paste with water in a mortar, and ground with more water. The liquor is decanted into a litre flask, and further addition of water is made to the residue in the mortar. After further grinding the liquor is again decanted, and finally the total quantity of sample is transferred to the flask, and made to 1000 cc.

The suspension is thoroughly shaken, and 100 cc. is immediately measured, and titrated with N/10 sodium arsenite, with stirring, until a drop extracted on the rod gives no blue colour with the starch-iodide paper; duplicate titrations are made.

EXAMPLE:

5.136 gm. of sample made to 1 litre.

100 cc. of suspension required 49.6 cc. N/10 arsenite solution.

1 cc. arsenite solution = 0.003546 gm. Cl., therefore 49.6 cc. = 0.17588 gm.
 = 0.17588 gm. Cl. in 100 cc. of suspension = 1.7588 gm. Cl. in
 1000 cc. suspension = 1.7588 gm. Cl. in 5.136 gm. of sample.

Therefore available chlorine = $1.7588 \times \frac{100}{5.136} = 34.24$ per cent.

Formalin

Formalin consists of an approximately 40 per cent. solution of formaldehyde in water, together with a small quantity of methyl alcohol to prevent polymerisation.

10 cc. of the sample is diluted to 500 cc. with water, and to 10 cc. of this solution is added 100 cc. of N/10 iodine solution. Sodium hydroxide solution is added until the excess of iodine is just decolorised, and the whole is stood for some minutes. The solution is then acidified with pure dilute hydrochloric acid, and the excess of iodine is titrated with N/10 sodium thiosulphate solution, using starch solution as an indicator. Each cc. of N/10 iodine solution absorbed corresponds to 0.0015 gm. of formaldehyde.

EXAMPLE :

Volume of sample taken = 10 cc.

The excess of iodine required 47.7 cc. of N/10 sodium thiosulphate solution. Therefore N/10 iodine solution absorbed = $100 - 47.7 = 52.3$ cc.

1 cc. N/10 iodine solution = 0.0015 gm. formaldehyde, therefore 52.3 cc. = 0.07845 gm. formaldehyde = 0.07845 gm. formaldehyde in 10 cc. of diluted solution = 3.922 gm. in 500 cc. = 3.922 gm. formaldehyde in 10 cc. of sample = 39.22 per cent. by volume.

Potassium and Sodium Permanganates

If solid, 5 gm. of the sample is dissolved in cold water, and made to 1 litre. 50 cc. of N/10 oxalic acid solution (6.303 gm. per litre) is warmed to 60° C.; 20 cc. of 10 per cent. sulphuric acid, which has been previously treated with permanganate to destroy its decolorising power, if any, is added, and the solution is titrated with the permanganate solution prepared above, or with a fluid preparation (diluted if necessary), until a permanent pink coloration is obtained. Each cc. of decinormal oxalic acid is equivalent to 0.00316 gm. of

potassium permanganate, 0.00284 gm. sodium permanganate ($\text{NaMnO}_4, 3\text{H}_2\text{O}$), or 0.0008 gm. of available oxygen.

Sulphur Dioxide Preparations

Sulphur dioxide is most readily estimated by titration with iodine solution.

A convenient amount of solution, or 2 gm. of solid preparation, is diluted with water, acidified with pure dilute hydrochloric acid, and titrated with N/10 iodine solution, using starch as indicator; each cc. of N/10 iodine solution required corresponds to 0.0032 gm. of sulphur dioxide.

Hydrogen Peroxide

The strength of hydrogen peroxide solutions is usually given in terms of the available oxygen which they contain. Thus a ten-volume solution is one containing ten times its volume of available oxygen. The estimation of hydrogen peroxide is made by titration with N/10 potassium permanganate solution, 3.1606 gm. KMnO_4 per litre; 1 cc. of this solution corresponds to 0.0017 gm. of H_2O_2 , and 0.0008 gm. or 0.560 cc. of available oxygen.

Process:

About 50 cc. of distilled water, in a flask, is acidified with 5 cc. of 10 per cent. sulphuric acid, and N/10 potassium permanganate is added until a faint permanent pink colour is obtained; with pure sulphuric acid this is immediate. 5 cc. of the solution to be examined is added, and the solution is titrated with the potassium permanganate solution until a pink colour again persists. From the above data the available oxygen can be calculated either to volume or weight.

Carbolic Powders

Carbolic powders consist chiefly of the calcium salts of phenol, cresol, and their homologues; neutral tar oils may be present, and the amount of lime present varies widely. An analysis usually estimates the free and combined acid tar oils and the neutral oil.

Free Acid Oil.—50 gm. of the sample is extracted by shaking

with about 150 cc. of ether in successive small portions ; the extract, which contains all the free oil, is shaken with 50 cc. of a 10 per cent. sodium hydroxide solution. The alkaline layer is separated, evaporated to half bulk, acidified with dilute sulphuric acid (equal volumes of concentrated acid and water), the whole being cooled the while, and the oil which separates is measured in a burette or a narrow measuring cylinder. This volume in cc. multiplied by 1.05 gives the weight of free acid oil, and is calculated to percentage.

Total Acid and Neutral Oil.—50 gm. of the sample is made into a paste with 50 cc. of water, and dilute hydrochloric acid (equal volumes of acid and water) is gradually added (with stirring and cooling) until the mixture is distinctly acid. The whole is then successively extracted with small quantities of ether, and each is decanted through a filter. The ether extracts are collected together in a flask, made alkaline, and 50 cc. of 10 per cent. sodium hydroxide solution is added with shaking. The ether contains the *neutral oil*, and is separated, evaporated, and the neutral oil weighed. The alkaline liquor is evaporated to 25 to 30 cc., cooled, acidified with dilute sulphuric acid, and the volume of the oil which separates is measured. This volume multiplied by 1.05 gives the *total acid oil*.

SOAP

SOAPS, in the commonly accepted sense of the word, are sodium and potassium salts of the fatty acids; the former are 'hard,' and the latter are 'soft' soaps. They are manufactured by boiling animal and vegetable fats and oils, and also resin, with alkali. In the case of the hard soaps the product passes through several processes of purification, and the glycerine is separated, but in the soft soaps all the material used is retained. Toilet soaps are milled, coloured, generally scented, and pressed; in some makes clarification is effected previously by solution in, and recovery from, alcohol, or by the addition of sugar. Modern practice has introduced a large number of medicated soaps, but many of these do not contain even a trace of the substances alleged. Castille soap is made from olive oil, and marine soap, which gives a lather with sea-water, is prepared from coconut oil. Soaps for particular use are also manufactured, containing sand and other inert substances.

The actual soap content of a sample is indicated by the quantity of acid radicle calculated as anhydride, *e.g.* a hard soap prepared from oleic acid will consist of sodium oleate, and the actual amount of soap present will be deduced from the quantity of oleic acid, calculated as anhydride, found. It is not necessary to separate the various fatty and resin acids which may be present in a sample; no marked error is introduced if the total fatty acids are multiplied by the common factor 0.9675 to express as total anhydrides.

Total Fatty Matter

5 gm. of the sample is placed in a separator, dissolved in hot water, and made cold. A few drops of methyl orange are added as indicator, and then dilute hydrochloric in slight excess; the total fatty and resin acids liberated are extracted

four times with ether. The ether extract is washed twice with water, evaporated to dryness, dried in an oven at 50° C., and weighed until constant. The amount found, multiplied by 0.9675, gives the total fatty matter expressed as anhydride.

Total Alkali

5 gm. of the sample is dissolved in water, and titrated with N/1 hydrochloric acid, using methyl orange as indicator. Alkali is calculated to Na_2O in the case of hard soaps, and to K_2O with soft soaps.

Free Caustic Alkali

25 gm. is dried, then extracted with absolute alcohol, and filtered; the residue is washed with further quantities of alcohol, and the total filtrate is titrated as above.

Alkaline Salts

The residue from above is washed with cold water, and the filtrate titrated as before.

Water

The water is best obtained by difference, $100 - (\text{percentage of total fatty matter and total alkali})$.

RAG FLOCK

RAG flock is used for stuffing mattresses, and in upholstery. It is manufactured from the refuse of the rag trade by tearing the cast-off clothing, old carpets, etc., in a machine. The product, frequently containing 50 per cent. or more of dirt, was in former years commonly sold without further treatment, but purification is now legally enforced. Presumption of cleanliness is afforded by a low soluble chlorine content.

By the Rag Flock Regulations, 1912, it is enacted that flock shall be deemed to conform to the standard of cleanliness for the purposes of the Rag Flock Act, when the amount of soluble chlorine in the form of chlorides, removed by thorough washing with distilled water at a temperature not exceeding 25° C., from not less than 40 gm. of a well-mixed sample, does not exceed 30 parts of chlorine per 100,000 parts of flock. The main difficulty in making an examination of flock is to obtain an average sample. For this purpose at least 50 gm. of average portions of the flock is selected, and cut into small pieces. This is extracted with three amounts of 250 cc. of distilled water at a temperature not exceeding 25° C. The extract is filtered, concentrated by evaporation to about 250 cc., and about 20 cc. of a decinormal solution of silver nitrate, or a corresponding amount of silver nitrate, to ensure an excess, is added. The precipitated silver chloride is filtered, washed with hot water, ignited and weighed. Care is taken to remove as much as possible of the precipitate from the filter before burning and igniting the paper, as silver chloride in the fused state may cover any reduced silver and protect it from the nitric and hydrochloric acids added later. The main bulk of the precipitate is brushed from the watch glasses, in which it has been meanwhile deposited, on to the ashed paper. A drop of nitric and one of hydrochloric acid is added, and the whole is gently

warmed; strong heating is avoided, as silver chloride volatilises at a comparatively low temperature. 143.34 parts of silver chloride represent 35.46 parts of chlorine, therefore the factor for the conversion of silver chloride to chlorine is 0.2474.

APPENDIX

ATOMIC WEIGHTS (OXYGEN=16), 1919-20

Element.	Sym- bol.	Weight.	Element	Sym- bol.	Weight.
Aluminium .	Al	27.1	Mercury .	Hg	200.6
Antimony .	Sb	120.2	Molybdenum	Mo	96.0
Argon .	A	39.90	Neon .	Ne	20.2
Arsenic .	As	74.96	Nickel .	Ni	58.68
Barium .	Ba	137.37	Nitrogen .	N	14.008
Bismuth .	Bi	208.0	Osmium .	Os	190.9
Boron .	B	10.9	Oxygen .	O	16.00
Bromine .	Br	79.92	Palladium .	Pd	106.7
Cadmium .	Cd	112.40	Phosphorus .	P	31.04
Calcium .	Ca	40.07	Platinum .	Pt	195.2
Carbon .	C	12.00	Potassium .	K	39.10
Cerium .	Ce	140.25	Radium .	Ra	226.0
Chlorine .	Cl	35.46	Selenium .	Se	79.2
Chromium .	Cr	52.0	Silicon .	Si	28.3
Cobalt .	Co	58.97	Silver .	Ag	107.88
Copper .	Cu	63.57	Sodium .	Na	23.00
Fluorine .	F	19.0	Strontium .	Sr	87.63
Gold .	Au	197.2	Sulphur .	S	32.06
Helium .	He	4.00	Tellurium .	Te	127.5
Hydrogen .	H	1.008	Thorium .	Th	232.15
Iodine .	I	126.92	Tin .	Sn	118.7
Iridium .	Ir	193.1	Titanium .	Ti	48.1
Iron .	Fe	55.84	Tungsten .	W	184.0
Krypton .	Kr	82.92	Uranium .	U	238.2
Lead .	Pb	207.20	Vanadium .	V	51.0
Lithium .	Li	6.94	Xenon .	Xe	130.2
Magnesium .	Mg	24.32	Zinc .	Zn	65.37
Manganese .	Mn	54.93			

Long Measure (Metric System)

1 metre	=	39.370113 inches.
1 millimetre	=	0.001 metre.
1 centimetre	=	0.01 „
1 decimetre	=	0.1 „
1 metre	=	1.0 „
1 decametre	=	10 metres.
1 hectometre	=	100 „
1 kilometre	=	1000 „
1 myriametre	=	10000 „
1 micron (μ)	=	0.001 millimetre.

Capacity (Metric System)

1 litre	=	1000 cubic centimetres.
1 millilitre	=	0.001 litre
1 centilitre	=	0.01 „
1 decilitre	=	0.1 „
1 litre	=	1.0 „
1 decalitre	=	10 litres.
1 hectolitre	=	100 „

Weight (Metric System)

1 gramme=the weight of 1 cubic centimetre of water at 4° C., and 760 millimetres barometric pressure.

1 milligramme	=	0.001 gramme.
1 centigramme	=	0.01 „
1 decigramme	=	0.1 „
1 gramme	=	1.0 „
1 decagramme	=	10 grammes.
1 hectogramme	=	100 „
1 kilogramme	=	1000 „

Measure of Capacity (British Pharmacopœia)

1 millilitre or mil. (Ml.)	=	1 cc.
1 decimil (Dl.)	=	0.1 cc.
1 centimil (Cl.)	=	0.01 cc.
1 litre (Lit.)	=	1000 cc.

CONVERSION TABLE

(Multiplication Factors)

Centimetres into inches	0.3937
Inches into centimetres	2.540
Millimetres into inches	0.0394
Inches into millimetres	25.40
Metres into inches	39.3701
Inches into metres	0.0254
Metres into feet	3.2808
Feet into metres	0.3048
Metres into yards	1.094
Yards into metres	0.9144
Square centimetres into square inches	0.155
Square inches into square centimetres	6.4516
Cubic centimetres into cubic inches	0.061
Cubic inches into cubic centimetres	16.387
Square metres into square yards	1.196
Square yards into square metres	0.836
Cubic metres into cubic yards	1.308
Cubic yards into cubic metres	0.765
Cubic centimetres into minims	16.894
Minims into cubic centimetres	0.059
Litres into pints	1.760
Pints into litres	0.568
Litres into gallons	0.220
Gallons into litres	4.546
Gallons into cubic feet	0.1605
Cubic feet into gallons	6.229
Grammes into ounces	0.035
Ounces into grammes	28.349
Grammes into grains	15.432
Grains into grammes	0.0648
Lbs. into grammes	453.592
Lbs. into grains	7000.00
Kilogrammes into lbs.	2.205
Lbs. into kilogrammes	0.454
Ounces into grains	437.5
Grains into minims	1.097
Minims into grains	0.911
Grammes per cubic metre into grains per cubic foot	0.4368

Grains per cubic foot into grammes per metre	.	.	2.2894
Parts per 100,000 into grains per gallon	.	.	0.7
Grains per gallon into parts per 100,000	.	.	1.429
Degrees Centigrade into degrees Fahrenheit	.	.	1.8+32
Degrees Fahrenheit into degrees Centigrade	.	-32 then $\times 0.555$	
Degrees Twaddle into specific gravity	.	.	$\times 5+1000$
Specific gravity to Twaddle	.	.	-1000×0.2

CONVERSION OF THERMOMETRIC SCALES

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
200	392.0	169	336.2	138	280.4	107	224.6
199	390.2	168	334.4	137	278.6	106	222.8
198	388.4	167	332.6	136	276.8	105	221.0
197	386.6	166	330.8	135	275.0	104	219.2
196	384.8	165	329.0	134	273.2	103	217.4
195	383.0	164	327.2	133	271.4	102	215.6
194	381.2	163	325.4	132	269.6	101	213.8
193	379.4	162	323.6	131	267.8	100	212.0
192	377.6	161	321.8	130	266.0	99	210.2
191	375.8	160	320.0	129	264.2	98	208.4
190	374.0	159	318.2	128	262.4	97	206.6
189	372.2	158	316.4	127	260.6	96	204.8
188	370.4	157	314.6	126	258.8	95	203.0
187	368.6	156	312.8	125	257.0	94	201.2
186	366.8	155	311.0	124	255.2	93	199.4
185	365.0	154	309.2	123	253.4	92	197.6
184	363.2	153	307.4	122	251.6	91	195.8
183	361.4	152	305.6	121	249.8	90	194.0
182	359.6	151	303.8	120	248.0	89	192.2
181	357.8	150	302.0	119	246.2	88	190.4
180	356.0	149	300.2	118	244.4	87	188.6
179	354.2	148	298.4	117	242.6	86	186.8
178	352.4	147	296.6	116	240.8	85	185.0
177	350.6	146	294.8	115	239.0	84	183.2
176	348.8	145	293.0	114	237.2	83	181.4
175	347.0	144	291.2	113	235.4	82	179.6
174	345.2	143	289.4	112	233.6	81	177.8
173	343.4	142	287.6	111	231.8	80	176.0
172	341.6	141	285.8	110	230.0	79	174.2
171	339.8	140	284.0	109	228.2	78	172.4
170	338.0	139	282.2	108	226.4	77	170.6

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
76	168.8	53	127.4	30	86.0	7	44.6
75	167.0	52	125.6	29	84.2	6	42.8
74	165.2	51	123.8	28	82.4	5	41.0
73	163.4	50	122.0	27	80.6	4	39.2
72	161.6	49	120.2	26	78.8	3	37.4
71	159.8	48	118.4	25	77.0	2	35.6
70	158.0	47	116.6	24	75.2	1	33.8
69	156.2	46	114.8	23	73.4	0	32.0
68	154.4	45	113.0	22	71.6	-1	30.2
67	152.6	44	111.2	21	69.8	-2	28.4
66	150.8	43	109.4	20	68.0	-3	26.6
65	149.0	42	107.6	19	66.2	-4	24.8
64	147.2	41	105.8	18	64.4	-5	23.0
63	145.4	40	104.0	17	62.6	-6	21.2
62	143.6	39	102.2	16	60.8	-7	19.4
61	141.8	38	100.4	15	59.0	-8	17.6
60	140.0	37	98.6	14	57.2	-9	15.8
59	138.2	36	96.8	13	55.4	-10	14.0
58	136.4	35	95.0	12	53.6	-11	12.2
57	134.6	34	93.2	11	51.8	-12	10.4
56	132.8	33	91.4	10	50.0	-13	8.6
55	131.0	32	89.6	9	48.2	-14	6.8
54	129.2	31	87.8	8	46.4	-15	5.0

MENSURATION FORMULÆ

l=length b=breadth. s=base. h=perpendicular height
from base.

r=radius. d=diameter. ch=chord. $\pi=3.1416$.

Area of a square $=s \times s$.
 „ rectangle $=l \times b$.
 „ triangle $=\frac{1}{2}(s \times h)$.
 „ parallelogram $=s \times h$.
 „ trapezoid $=\frac{1}{2}$ sum of parallel sides $\times h$
 between them.

Length of circumference of a circle $=d \times \pi$.

Area of a circle $=r^2 \times \pi$.

Area of an ellipse $=\text{long axis} \times \text{short axis} \times 0.7854$.

Area of a segment of a circle $=(ch \times \frac{2}{3}h) + \frac{h^3}{2ch}$.

Length of circumference of an ellipse $=\frac{1}{2}(\text{long axis} + \text{short axis}) \times \pi$.

Volume of a cube or rectangular vessel	$=l \times b \times h.$
Area of surface of a sphere	$=4 \times \pi \times r^2.$
Volume of a sphere	$=\frac{4}{3} \times \pi \times r^3.$
Area of surface of a cylinder	$=(2 \times \pi \times r \times h) + (2 \times \pi \times r^2).$
Volume of a cylinder	$=\pi \times r^2 \times h.$
„ pyramid	$=\frac{1}{3} \text{ (area of } s \times h).$
„ cone	$=\frac{1}{3} \text{ (area of } s \times h).$

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